

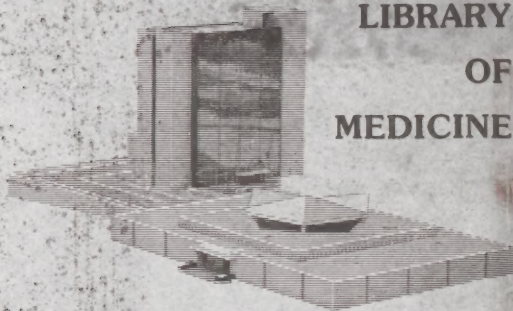


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A TEXT-BOOK  
OF  
ORGANIC CHEMISTRY.

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A TEXT-BOOK  
OF  
**Inorganic Chemistry.**

BY PROF. VICTOR von RICHTER,  
*University of Breslau.*

AUTHORIZED TRANSLATION,

BY EDGAR F. SMITH, M.A., Ph.D.,  
*Prof. of Chemistry in Wittenberg College, Springfield, Ohio; formerly  
in the Laboratories of the University of Pennsylvania and Muhlen-  
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and Paris, of the Academy of Natural Sciences of  
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CHEMISTRY  
OF THE  
CARBON COMPOUNDS;  
OR,  
ORGANIC CHEMISTRY.

BY  
✓  
PROF. VICTOR VON RICHTER,  
UNIVERSITY OF BRESLAU.

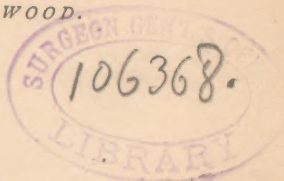
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# PREFACE

TO THE

## AMERICAN EDITION.

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The favorable reception of the American translation of Prof. von Richter's *Inorganic Chemistry* has led to this translation of the "*Chemistry of the Compounds of Carbon*," by the same author. In it will be found an unusually large amount of material, necessitated by the rapid advances in this department of chemical science. The portions of the work which suffice for an outline of the science are presented in large type, while in the smaller print is given equally important matter for the advanced student. Frequent supplementary references are made to the various journals containing original articles, in which details in methods and fuller descriptions of properties, etc., may be found. The volume thus arranged, will answer not only as a text-book, and indeed as a reference volume, but also as a guide in carrying out work in the organic laboratory. To this end numerous methods are given for the preparation of the most important and the most characteristic derivatives of the different classes of bodies.





# TABLE OF CONTENTS.

## INTRODUCTION.

Organic Chemistry Defined, 9. Elementary Organic Analysis, 10. Determination of Nitrogen, 14. Determination of the Molecular Formula, 18. Vapor Density Determination, 20.  
Chemical Structure of the Carbon Compounds, 23. Radicals and Formulas, 30. Early Theories upon the Constitution of Carbon Compounds, 32. Physical Properties, 34. Specific Gravity, 35. Melting Points—Boiling Points, 37. Optical Properties, 39.

## SPECIAL PART.

### CLASS I. FATTY BODIES OR METHANE DERIVATIVES.

Hydrocarbons, 44.

Hydrocarbons  $C_nH_{2n+2}$ , 45. Petroleum, 51. Paraffins, 52. Unsaturated

Hydrocarbons  $C_nH_{2n}$ , 53. Hydrocarbons  $C_nH_{2n-2}$ —Acetylene Series, 60.

Halogen Derivatives of Hydrocarbons, 64.

Compounds  $C_nH_{2n+1}X$  — Alkyllogens, 66. Compounds  $C_nH_{2n-1}X$ , 69.

Allyl Iodide, 71.

Compounds  $C_nH_{2n}X_2$ , 71. Chloroform, 74.

Glyceryl Bromide, 76. Nitro-derivatives, 77.

Nitro-paraffins, 79. Nitrolic Acids, 80.

Pseudo-nitrols, 82. Nitroform, 83.

Alcohols, Acids and their Derivatives, 84.

#### Monovalent Compounds.

Monovalent Alcohols, 87.

Structure of Monovalent Alcohols, 87. Formation of Alcohols, 89. Properties and transpositions, 92.

Alcohols  $C_nH_{2n+1}.OH$ . Methyl Alcohol, 94. Ethyl Alcohol, 94. Propyl Alcohols, 96. Butyl Alcohols, 97. Amyl Alcohols, 98. Ethal, 102.

Unsaturated Alcohols, 103. Allyl Alcohol, 103. Propargyl Alcohol, 104.

Ethers, simple and mixed, 105. Ethyl Ether, 107.

Mercaptans and Thio-ethers, 108. Sulphuric Acids, 111. Alkyl Sulphines, 112. Selenium and Tellurium Compounds, 113.

Esters of Mineral Acids, 113. Esters of Nitric Acid, 115. Esters of Sulphuric Acid, 116. Esters of Sulphurous Acid, 118. Sulpho-Acids, 119. Esters

of Boric Acid, 121. Esters of the Phosphoric Acids, 121. Phosphinic Acids, 122. Esters of Arsenic Acid, 122. Esters of Silicic Acid, 122.

### Amines, 122.

Primary, 126. Secondary, 127. Tertiary, 128. Nitroso amines, 128. Ammonium Bases, 128.

### Hydrazines, 129.

### Phosphines or Phosphorus Bases, 131.

### Arsenic Bases, 133.

Antimony Compounds, 137. Boron Compounds, 138. Silicon Compounds, 138.

### Metallo-Organic Compounds, 139.

Compounds of the Alkali Metals, 141. Zinc Compounds, 141. Mercury Compounds, 143. Aluminium Compounds, 144. Tin and Lead Compounds, 145. Bismuth Compounds, 148.

### Aldehydes and Ketones, 148.

Aldehydes, 149. Aldoxims, 152. Aldehydes of Paraffin Series—Methyl Aldehyde, 152. Acetaldehyde, 153. Condensation of Aldehydes, 154. Chloral, 156. Thioaldehyde, 157. Amyl Aldehydes, 158.

Unsaturated Aldehydes, Allyl Aldehyde, 158. Crotonaldehyde, 159.

Ketones, 160. Acetone, 162. Acetoxims, 163. Glyoxims, 164. Condensation of Acetone, 165. Phorone, 165. Acetone Bases, 165. Acetone Homologues, 166.

### Monobasic Acids, 168.

Fatty Acids  $C_nH_{2n}O_2$ , 171. Formic Acid, 173. Acetic Acid, 175. Substituted Acetic Acids, 177. Propionic Acid, 178. Butyric Acids, 181. Valeric Acids, 183. Hexoic Acids, 185. Heptoic Acids, 185. Higher Fatty Acids, 185. Soaps, 186. Stearic Acid, 187.

Unsaturated Acids  $C_nH_{2n-2}O_2$ , 188. Acrylic Acid, 190. Crotonic Acids, 192. Angelic Acid, 193. Oleic Acid, 195. Linoleic Acid, 196.

Acids  $C_nH_{2-4}O_2$ : Propiolic Acid, 197.

The Acid Haloids, 198. Acetyl Chloride, 199.

Cyanides of Acid Radicals, 200.

Acid Anhydrides, 200. Thio-acids and Thio-anhydrides, 202.

Esters of the Fatty Acids, 203. Spermaceti, Beeswax, 206.

Acid Amides, 207. Amide-chlorides, 209. Thio-amide, 209.

Cyan-, sulpho-, and Amido-derivatives of Acids, 211.

Ketone Alcohols, 213. Acetyl Carbinol, 213.

Ketonic Acids,  $\alpha$ -Ketonic Acids, 214. Pyroracemic Acid, 214.  $\beta$ -Ketonic Acids, 216. Aceto-acetic Ester, 219.  $\gamma$ -Ketonic Acids, 224. Lævulinic Acid, 224.

### Cyanogen Compounds, 226.

Dicyanogen, 226. Hydrocyanic Acid, 228. Halogen Compounds of Cyanogen, 229. Metallic Cyanides, 230. Nitroprussides, 232.



Cyanic Acids, 233. Cyanuric Acids, 234. Esters of Cyanic Acids or Cyanetholins, 235. Isocyanic Esters, 235. Esters of Cyanuric Acids, 237. Thiocyanic Acids, 237. Esters of Thio- and iso-thiocyanic Acids, 239. Allyl Mustard Oil, 241.

Cyanides of Alcohol Radicals, Nitriles, 241.

Acetonitrile, 243. Mercury Fulminate, 245. Fulminuric Acid, 245. Isocyanides or Carbylamines, 246.

Amide Derivatives of Cyanogen, 247. Imido-ethers, 248. Amidines, 249.

Guanidines, 250. Guanamines, 252.

### Divalent Compounds, 252.

Divalent (dihydric) Alcohols or Glycols, 252. Methylene Derivatives, 256.

Ethylene Glycol, 256. Ethylene Oxide, 257. Glycolyl Aldehyde, 258.

Ethidene Compounds, 259. Propylene Glycols, 260. Butylene Glycols, 261.

Aldol, 261. Pinacone, 262. Amines of Divalent Radicals, 263. Oxy-ethyl

Bases, 264. Alkines, alkeïnes, 264. Choline, 265. Betaine, 265. Sul-

phonic Acids of Divalent Radicals, 266. Isethionic Acid, 267. Taurine,

267. Ethidene Sulphonic Acids, 268.

Divalent Monobasic Acids, 269.  $\alpha$ -,  $\beta$  and  $\gamma$ -oxy-acids, 272. Their Decomposition, 274. Anhydrides of Oxy-acids, 274. Lactones, 275.

Oxy-Fatty Acids  $C_nH_{2n}O_3$ , 276. Glycollic Acid, 276. Glyoxal, 279. Glyoxalins, 279. Glyoxylic Acid, 280. Lactic Acids, 281. Chloralides, 284.

Hydracrylic Acid, 285. Oxybutyric Acid, 286. Oxyvaleric Acids, 287.

Amides of Divalent Acids, 289. Amido-acids, 289.

Glycocoll, 291. Alanine, 293. Leucine, 294. Carbonic Acid and Derivatives, 294. Esters of Carbonic Acid, 296. Trithio-carbonic Acid, 298.

Dithio-carbonic Acid, 298. Xanthic Acids, 298. Amide Derivatives, 300.

Urethanes, 300. Dithio-urethanes, 302. Thiourethanes, Esters of sulpho-carbamic acid, 302.

Urea, 303. Compound Ureas, 305. Ureïdes, 307. Hydantoïn, 307. Allophanic Acid, 309. Thiourea, 309. Sulpho-hydantoïn, 312.

Guanidine Derivatives, 312. Creatine, 313.

### Dibasic Acids, 314. Anhydrides, 316.

Oxalic Acid, 318. Amides of Oxalic Acid, 320. Malonic Acid, 321. Mesoxalic acid, 323. Succinic Acids, 324. Succinimide, 326. Pyrotartaric

Acids, 329. Adipic Acid, 331. Suberic Acid, 333.

Unsaturated Dibasic Acids, 333.

Fumaric and Maleïc Acids, 334. Itaconic Acid, 338. Teraconic Acid, 339.

Acetylene Dicarboxylic Acid, 339.

Carbamides of Dibasic Acids, 340. Parabanic Acid, 340. Barbituric Acid, 342. Alloxan, 344. Uric Acid, 346. Guanine, 348. Caffèine, 349.

### Trivalent Compounds, 350.

Trivalent Alcohols, 351. Glycerol, 352. Haloid Esters of Glycerol, 354. Glycide Compounds, 355. Alcohol Ethers of Glycerol, 357. Acid Esters of Glycerol, 357.

**Trivalent Monobasic Acids.** Glyceric Acid, 359.

**Dibasic Mono-oxy-Acids.** Tartronic Acid, 360. Malic Acid, 361. Amides of Malic Acid, 362. Asparagine, 363.

Oxy-pyrotartaric Acids, 363. Paraconic Acid, 364.

Terebic Acid, 365.

**Tribasic Acids.** Formyl Tricarboxylic Acid, 366. Tricarballic Acid, 367. Aconitic Acid, 367. Chelidonic Acid, 368. Meconic Acid, 368.

### **Tetravalent Compounds.**

**Tetravalent Alcohols,** 368, Erythrol, 369.

**Monobasic Acid.** Erythritic Acid, 369.

Dibasic Acids. Tartaric Acid, 369. Racemic Acid, 372.

**Tribasic Acids.** Carboxytartronic Acid, 373. Citric Acid, 373.

**Tetrabasic Acids.** Acetylene Tetracarboxylic Acid, 374.

**Pentavalent Compounds.**

Quercite, 374. Saccharin, 375. Aposorbic Acid, 376. Desoxalic Acid, 386.

**Hexavalent Compounds.**

Mannitol, 376. Dulcitol, 377. Mannitic Acid, 378. Gluconic Acid, 378.

Dioxytartaric Acid, 378. Saccharic Acid, 379. Mucic Acid, 379.

**Carbohydrates,** 380. Glucoses, 384. Cane Sugar, 387. Milk Sugar, 388.

Maltose, 389. Starch, 390. Gums, 390. Cellulose, 391. Pyroxylin, 392.

**Trimethylene Group.**

Trimethylene, 393. Trimethylene Carboxylic Acid, 393. Aceto-trimethylene Carboxylic Acid, 394.

**Tetramethylene Derivatives.**

Tetramethylene Carboxylic Acid, 394. Aceto-tetramethylene, 395.

**Furfuryl Group.**

Furfuran, Furfural, 395. Pyromucic Acid, 397.

**Thiophene Group.**

Thiophene, 398. Thiophenic Acid, 399. Thiotolene, 399.

**Pyrrol Group.**

Pyrrol, 399. Pyrrol Homologues, 401. Pyrrol Carboxylic Acid, 502. Pyrrolin, 402.

## **CLASS II. BENZENE DERIVATIVES.**

Benzene Nucleus, 403. Isomerism of Benzene Derivatives, 405. Structure of Same, 405. Addition Products, 411.

**Hydrocarbons,**  $C_n H_{2n-6}$ , 411.

Benzene, 414. Toluene, 414. Xylenes, 415. Mesitylene, 416. Cumene, 417. Durene, 418. Cymene, 419. Hexamethyl Benzene, 420.

**Halogen Derivatives of the Hydrocarbons,** 420.

Chlor-benzenes, 422. Chlortoluenes, 424. Benzyl Chloride, 424.

**Nitro-derivatives of Hydrocarbons, 426.**

Nitrobenzene, 426. Nitro-chlorbenzenes, 427. Nitro-toluenes, 429.

**Nitroso-Compounds, 430.****Amido-Compounds, 430.**

Aniline, 433. Substituted Anilines, 434. Nitranilines, 436. Alcoholic Anilides, 437. Dimethyl Aniline, 438. Diphenylamine, 439. Thiodiphenylamine, 440. Methylene Blue, 430. Acid Anilides, 441. Acetanilide, 442. Diphenyl Urea, 443. Phenyl Urethanes, 444. Phenyl Mustard Oil, 445. Phenyl-thiourethane, 446. Phenylthiurea, 447. Phenylthiohydantoin, 449. Phenyl Guanidines, 449. Phenyl Amidines, 450.

Phenyl Phosphines, 451. Mercury Phenyl, 452. Toluidines, 452. Xyldines, 453.

Diamido-Compounds, 453. Condensation Products, 454.

**Diazo-Compounds, 455.**

Azo-Compounds, 452. Amido-azo-compounds, 463. Azo-dyes, 468. Safranines and Indulines, 469.

**Hydrazine-Compounds, 471.**

Sulpho-compounds, of the Hydrocarbons, 473. Benzene Sulphonic Acid, 475.

Nitrobenzene Sulphonic Acids, 477. Amidobenzene Sulphonic Acids, 477.

Toluene Sulphonic Acids, 478.

**Phenols, 478.**

Monovalent Phenols, 481. Phenol, 481. Chlor-phenols, 484. Nitroso-phenol, 486. Nitro-phenols, 487. Picric Acid, 488. Amido-phenols, 489. Carbamido-phenols, 490. Amido-thiophenol, 491. Phenol-sulphonic Acids, 492.

Cresols, 493. Xylenols, 494. Thymol, 494. Carvacrol, 495.

Divalent Phenols, 495. Pyrocatechin, 495. Resorcin, 496. Hydroquinone, 497. Orcin, 498. Litmus, 499. Creosol, 500.

Trivalent Phenols, 500. Pyrogallie Acid, 500. Phloroglucin, 501. Oxyhydroquinone, 501. Phenose, 502.

**Quinones, 502.**

Quinone, 503. Chloranil, 503. Toluquinone, 504. Quinone-chlorimides, 505. Indophenols, Indoanilines, 505.

**Alcohols, 507.**

Benzyl Alcohol, 507. Toly Alcohol, 508.

Divalent Alcohols, 509. Benzoyl Carbinol, 510. Phenol Alcohols, Saligenin, 510.

Phenyl Glycerol, 511.

Aldehydes, 511. Benzaldehyde, 513. Amarine, Lophine, 514. Amidobenzaldehydes, 516. Cumic Aldehyde, 518.

Oxy-aldehydes, 518. Salicylic Aldehyde, 519. Anisic Aldehyde, 520. Protocatechuic Aldehyde, 520. Vanillin, 521. Piperonal, 521.

**Ketones, 521.** Acetophenone, 521. Amidoacetophenone, 523.

**Nitriles, 524.** Benzonitrile, 525. Benzyl Cyanide, 526.

Benzimido-ethers, 526. Benzenylamidines, 527.

### **ACIDS, 527.**

**Monobasic Acids, 531.**

Benzoic Acid, 531. Hippuric Acid, 533. Halogen Benzoic Acids, 534. Nitro-benzoic Acids, 535. Amido-benzoic Acids, 535. Anthranilic Acid, 536. Chrysanic Acid, 537. Azo-benzoic Acids, 537. Diazobenzoic Acids, 538.

Toluic Acids, 539. Phenyl-acetic Acid, 540. Lactams and Lactims, 541.

Xylic Acids, 542. Hydrocinnamic Acid, 543. Phenylalanine, 543. Hydrocarbostyryl, 544. Cuminic Acid, 545.

**Ketonic Acids, 546.** Phenylglyoxylic Acid, 546. Isatinic Acid, 546. Benzoyl-acetic Acid, 547. Phthalyl Acetic Acid, 548.

Mono-oxy-acids, 548. Salicylic Acid, 549. Oxybenzoic Acid, 550. Paraoxybenzoic Acid, 551. Anisic Acid, 551.

Cresotinic Acids, 552. Phthalid, 552. Mandelic Acid, 552. Tyrosine, 554. Phenyl-lactic Acids, 556. Oxycinnamic Acids, 557.

Dioxy-acids, 557. Protocatechuic Acid, 558. Trioxy-acids, 562. Gallic Acid, 562. Tannic Acids, 563. Quinic Acid, 564.

### **Dibasic Acids, 565.**

Phthalic Acid, 565. Isophthalic Acid, 566. Terephthalic Acid, 566. Uvic Acid, 567. Oxy-di-carboxylic Acids, 668. Meconine, 569.

**Tribasic Acids:** Trimellitic Acid, 569.

**Tetrabasic Acids:** Pyromellitic Acid, 570.

**Hexabasic Acids:** Mellitic Acid, 570.

### **Unsaturated Compounds.**

Styrolene, 572. Phenyl Acetylene, 573. Styryl Alcohol, 574. Cinnamic Acid, 576. Atropic Acid, 580. Phenyl-propionic Acid, 581. Coumaric Acid, 584. Coumarin, 585. Umbelliferon, 587. Piperic Acid, 588. Benzmalonic Acid, 588.

### **Indol Group.**

Indol, 589. Oxindol, 591. Isatin, 594. Isatoxims, 596.

Indigo-blue, 597. Indigo-carmin, 600.

Derivatives with Several Benzene Nuclei, 600.

### **(1) Derivatives of Directly Combined Nuclei. Diphenyl Group.**

Diphenyl, 600. Benzdine, 601.

Carbazol, 602. Coeroulignone, 602. Diphenic Acid, 604.

Diphenylene Derivatives, 604. Fluorene, 605.

Ditolyl, 606. Diphenyl Benzene, Triphenyl Benzene, 606.

- (2) **Derivatives of Benzene Nuclei Joined by one Carbon-atom.**  
 Diphenyl Methane Derivatives, 606.  
 Diphenyl Methane, 609. Benzophenone, 610. Diphenyl Ethanes, 611. Diphenyl Acetic Acid, 611. Benzilic Acid, 612. Phenyl-tolyl Methanes, 612. Benzoyl-benzoic Acids, 613.  
 Triphenyl Methane Derivatives, 614.  
 Triphenyl Methane, 614. Diphenyltolyl Methane, 615.  
 Amido-derivatives. Malachite-green, 617. Rosaniline, 618. Alkyllic Rosanilines, 621.  
 Phenol Derivatives. Aurin, 624. Rosolic Acid, 625.  
 Carboxyl Derivatives, 625. Phthalophenone, 626. Phthaleins, 627. Phthalins, 628. Fluorescein, 629. Coerulein, 629.
- (3) **Derivatives of Benzene Nuclei Joined by two Carbon-atoms.**  
 Dibenzyl Group.  
 Dibenzyl Group, 629. Stilbene, 630. Hydrobenzoins, 631. Benzoin, 631. Pinacones and Pinacolines, 633. Carboxyl Derivatives, 633. Tetraphenyl Ethane, 634. Vulpic Acid, 635.  
 Anthracene Group, 635.  
 Anthracene, 637. Oxyanthracenes, 638. Phthalidins and Phthalideins, 638.  
 Anthraquinone, 638. Oxyanthraquinones, 639. Dioxyanthraquinones: Alizarin, 640. Chrysazin, 642. Trioxyanthraquinones: Purpurin, 642.  
 Alkyllic Anthracenes, 643. Methyl Anthracene, 643. Chrysophanic Acid, 643. Anthracene Carboxylic Acids, 644.  
 Hydrindonaphthene, 644.
- (4) **With Condensed Benzene Nuclei.**  
 Naphthalene, 645. Homologous Naphthalenes, 648. Acenaphthene, 648.  
 Amidonaphthalenes, 649. Naphthalene Red, 650. Naphthols, 651. Naphthoquinones, 653. Naphthalene-alizarin, 653. Naphthoic Acids, 654.  
 Phenanthrene, 655. Phenanthraquinone, 656. Fluoranthene, 657. Pyrene, 657. Chrysene, 657. Retene, 658. Picene, 658.  
 Pyridine and Quinoline Groups.  
 (1) Pyridine Group, 659. Pyridine, 662. Methyl Pyridines, 663. Collidines, 663. Pyridine Monocarboxylic Acids, 664. Pyridine Tricarboxylic Acids, 666.  
 (2) Quinoline Group, 667. Quinoline, 669. Oxyquinolines, 670. Lepidine, 672. Quinoline Carboxylic Acids, 673.  
 Complex Nuclei Containing Nitrogen.  
 Naphtho-quinolines, 675. Pnenanthrolines, 675. Anthraquinoline, 675.  
 Acridines, 675. Chrysaniline, 676.  
 Cinnolin and Quinoxaline Derivatives, 676.  
 Oxyquinizine Derivatives, 676. Antipyrine, 677.
- Alkaloids:** Piperidine, 677. Coniine, 678. Nicotine, 679.  
 Opium Bases: Morphine, 679. Narcotine, 679.



Cinchona Bases: Quinine, 680. Cinchonine, 680.

Strychnine Bases: Strychnine, 681. Brucine, 681.

Solanum Bases: Atropine, 681, Tropine, 682. Tropeïnes, 682.

**Terpenes:** Oil of Turpentine, 683. Camphenes, 684. Citrene, 684.

**Camphors:** Japan Camphor, 685. Borneo-camphor, 686. Mentho-camphor, 686. Camphoric Acid, 686.

**Resins:** Colophony, 687. Amber, 687. Gum Resins, 687.

Glucosides: Æsculin, 688. Arbutin, 688. Quercitrin, 688. Myronic Acid, 688.

Bitter and Coloring Substances: Aloes, 689. Santonin, 689. Curcumin, 689.

Hæmatoxylin, 689, Carminic Acid, 689. Chlorophyll, 690.

Biliary Substances, 690. Cholesterine, 690. Gelatines, 690. Glutin, 691.

Albuminates: Albumen, 691, Fibrin, 691. Casein, 691. Oxyhæmoglobin, 694. Lecithin, 694.



## ERRATA.

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- Page 13, seventh line from bottom, read *B*, instead of *Berichte*.
- “ 30, nineteenth line from bottom, read *law of even numbers*, instead of *conjugate atomic numbers*.
- “ 94, twenty-seventh line from top, read *Ber. 13*, for *Ber. 73*.
- “ 137, fourteenth line from bottom, read *regarded as croton-chloral*, instead of *obtained from crotonaldehyde*.
- “ 159, eighth line from top, read  $\alpha,\beta$ -*dibrompropionic acid*, instead of  $\beta$ -*dibrompropionic acid*.
- “ 190, seventh line from top, read  $PCl_3$ , for  $PCl_5$ .
- “ 193, seventeenth line from bottom, read  $PCl_3$ , for  $PCl_5$ .
- “ 357, twentieth line from top, read *glycerol*, instead of *glycercol*.
- “ 458, fifteenth line from top, read  $C_6H_6$ , for  $C_6H_5$ .
- “ 574, eighth line from top, read *diphenyl-diacetylene*, instead of *phenyl-diacetylene*.

# A TEXT-BOOK OF ORGANIC CHEMISTRY.

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## INTRODUCTION.

The chemistry of the carbon compounds was formerly called *Organic Chemistry*. This designation originated in the time of Lavoisier (1743-1794), who announced the fundamental ideas of the nature of the chemical elements and compounds. He it was, too, who first recognized the true composition of the so-called *organic* substances occurring in the organism of plants and animals. He discovered that by their combustion, carbon dioxide and water were always formed, and showed that the component elements were generally carbon, hydrogen and oxygen, to which sometimes—especially in animal substances—nitrogen was added. Lavoisier further gave utterance to the opinion that peculiarly constituted atomic groups, or radicals, were to be accepted as present in organic substances; while the mineral substances were regarded by him as the direct combinations of single elements.

In this way it was proved that the substances peculiar to the plant and animal kingdoms possess a composition different from that of mineral matter. As, however, it seemed impossible, for a long time, to prepare the former from the elements synthetically, the opinion prevailed that there existed an essential difference between the organic and inorganic substances; and this led to the distinction of the chemistry of the first as Organic Chemistry, and that of the second as Inorganic Chemistry. The prevalent opinion was, that the chemical elements in the living bodies were subject to other laws than those in the so-called inanimate nature, and that the organic substances were formed only in the organism by the intervention of a peculiar vital force, and that they could not possibly be prepared in an artificial way.

One fact sufficed to prove these limitations, depending upon negative results, to be unfounded. The first organic substance artificially prepared was urea (Wöhler, 1828). By this synthesis chiefly, to which others were soon added, the idea of a peculiar force necessary to the formation of organic compounds, was

contradicted. However, even as late as 1840, Gerhardt clung to the view that chemical forces only exercise a destroying action, and with Berzelius, defined organic substances as those produced by vital force. Numerous additional syntheses soon showed that such opinions were no longer tenable. All further attempts to separate organic substances from the inorganic were futile. At present we know that these do not differ essentially from each other; that the peculiarities of organic compounds are dependent solely on the nature of their essential constituent, Carbon; and that all substances belonging to plants and animals, can be artificially prepared from the elements.

*Organic Chemistry* is, therefore, the *chemistry of the carbon compounds*. Its separation from general chemistry is demanded by practical considerations; it is occasioned by the very great number of carbon compounds.

We would here note the difference between the conceptions of *organic* and *organized* bodies. Different carbon compounds possess the power to assume in the living organisms an organized structure—to form cells. The causes and conditions of this power are as yet unknown to us. We know no more of them than of the cause of the union of molecules to form crystals, or of the atoms to form molecules.

Further, notice that organic chemistry does not occupy itself with the investigation of the chemical processes in vegetable and animal organisms. This is the office of *Physiological Chemistry*.

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## COMPOSITION OF CARBON COMPOUNDS.

### ELEMENTARY ORGANIC ANALYSIS.

Most carbon compounds occurring in vegetables and animals consist of carbon, hydrogen, and oxygen. Many, also, contain nitrogen, and on this account these elements are termed *Organogens*. Sulphur and phosphorus are present in some naturally occurring substances. Almost all the elements, metalloids and metals, may be artificially introduced as constituents of carbon compounds in direct union with carbon. The number of known carbon compounds is exceedingly great, while the possible ones are almost without limit. The general procedure, therefore, of isolating the several compounds of a mixture, as is done in mineral chemistry in the separation of bases from acids, is impracticable. The mixtures occurring in vegetable and animal bodies, are only separated by special methods. The task of elementary organic analysis is to determine, qualitatively and quantitatively, the elements of a carbon compound after it has been obtained in a pure state and charac-



terized by definite properties. The analysis is generally limited to the determinations of carbon, hydrogen, and nitrogen. Simple practical methods for the direct determination of oxygen do not exist. Its quantity is usually calculated by difference, after the other constituents have been found.

#### DETERMINATION OF CARBON AND HYDROGEN.

The presence of carbon in a substance is shown by its charring when ignited away from air. Ordinarily its quantity, as also that of the hydrogen, is ascertained by combustion. The substance is mixed in a glass tube with copper oxide and heated. Carbon burns to carbon dioxide, the hydrogen to water. In quantitative analysis, these products are collected in separate vessels, and the increase in weight of the latter determined. Carbon and hydrogen are always

FIG. 1.



simultaneously determined in one operation. The details of the quantitative analysis are fully described in the text-books of analytical chemistry. It is only necessary here, therefore, to outline the methods employed. As a usual thing, the combustion is effected by the aid of copper oxide in a difficultly fusible glass tube, fifty to sixty centimetres long, and drawn into a point at one end (Fig. 1).

Dry, freshly ignited, granular copper oxide is first introduced into the tube (from *a* to *b*); then the mixture of the solid substance

FIG. 2.

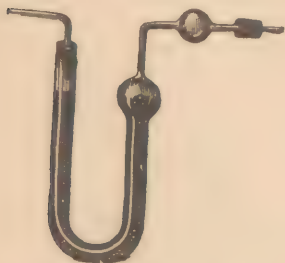


FIG. 3.

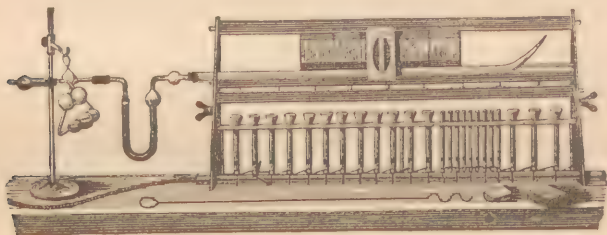


(about 0.2–0.3 gr.) with pulverized cupric oxide (*b* to *c*), and afterwards granular copper oxide (to *d*), upon which is placed a wad of asbestos. If the substance to be analyzed is a liquid, it is

weighed out in a glass bulb drawn out to a point, and this placed in the combustion tube. When the latter has been filled, the open end is closed with a cork, carrying a straight or bent calcium chloride tube (Fig. 2).

This is filled with dried granulated chloride of calcium, which absorbs the aqueous vapor produced in the combustion tube, while the carbon dioxide passes on unchanged. To the calcium chloride tube is attached, by means of rubber tubing, a Liebig bulb (Fig. 3), containing potassium hydrate (of sp. gr. 1.27); the potash bulb of Geissler is better. The carbon dioxide formed in the combustion is absorbed in this. To the potash bulb there is also attached a small tube; this is filled with stick potash. It serves to retain the slight quantity of aqueous vapor which might escape from the bulbs. Before the combustion takes place, the calcium chloride tube and the apparatus containing potassium hydrate (also the small tube) are weighed separately. Their

FIG. 4.



connection is then made, and the combustion tube placed in the furnace. The arrangement of the apparatus is illustrated in Fig. 4.

The front and back portions of the combustion tube are heated first. These parts contain only pure cupric oxide. Subsequently the middle portion containing the substance is gradually and partially heated. The heat should be so applied that the liberated carbon dioxide enters the potash bulbs in separate bubbles. The combustion is complete when this no longer occurs. The flames are then extinguished, the drawn-out end of the tube is connected, by means of rubber tubing, with a drying apparatus; the point of the tube is broken off and air drawn through, to remove all aqueous vapor and carbon dioxide from the combustion tube, and to bring them into their proper absorption vessels (the drying apparatus removes moisture and carbon dioxide from the aspirated air). When the substance is difficult to burn, it is advisable finally to conduct a stream of oxygen through the combustion tube, in order that all the carbon may be converted into carbon dioxide. After the com-

bustion tube has become cool, the apparatus is disconnected, and the various pieces weighed separately. The increase in weight of the calcium chloride tube represents the quantity of water produced; that of the potash bulbs, the amount of carbon dioxide. From these we can readily calculate the quantity of carbon and hydrogen in the substance analyzed.

Instead of mixing the substance with cupric oxide, it may be placed in a porcelain or platinum boat, then introduced into a tube open at both ends. The combustion in this case is carried out in a stream of air or oxygen—method of Glazer (Fig. 5).

A layer of granular copper oxide fills the tube from *d* to *e* (enclosed by two asbestos wads). This is ignited in a current of air, then allowed to cool. The end (*f*) is connected with the usual apparatus, previously weighed; the boat containing the substance (*c*) is introduced at the opposite end, and the latter joined either to an oxygen gasometer or some apparatus for purifying gases. The layer of cupric oxide is brought to a red heat, and the combustion executed in a slow current of air or oxygen. To avoid a diffusion of the gases backward in the tube, there is placed immediately behind the boat a wad (*b*) of asbestos or some copper; or a layer of mercury

FIG. 5.



is introduced between the drying apparatus and the combustion tube. A second analysis may be commenced as soon as the first is ended.

In this last method, platinum black (mixed with asbestos) may be substituted for cupric oxide:—method of Kopfer. A much shorter and more simple combustion furnace may then be employed. The method is adapted to the combustion of compounds containing the halogens (*Zeitschrift für anal. Chemie*, 1878, *Berichte*, 17, 1).

When nitrogen is present in the substances burned, oxides of it are sometimes produced, and these are absorbed in the calcium chloride tube and potash bulbs. To avoid this source of error, the oxides must be reduced to nitrogen. This may be accomplished by conducting the gases of the combustion over a layer of metallic copper, which, in form of filings or spiral, is placed in the front portion of the combustion tube. The latter, in such cases, should be a little longer than usual. The copper is previously reduced in a current of hydrogen, then ignited, when it often includes hydrogen, which subsequently becomes water. To remedy this, the copper heated in a current of hydrogen is raised to a temperature of  $200^{\circ}$  in an air-bath, or better, in a current of carbon dioxide or in a vacuum. Its reduction by the vapors of formic acid or methyl alcohol is more advantageous; this may be done by pouring a small quantity of these liquids into a dry test tube and then suspending in them the roll of copper heated to redness; copper thus reduced is perfectly free from hydrogen.

In the presence of chlorine, bromine or iodine, halogen copper compounds ( $\text{CuX}$ ) arise. These are somewhat volatile and pass over into the calcium

chloride tube. The placing of a spiral of copper or silver in the front part of the tube will obviate this. The presence of sulphur in the organic compound will afford, during combustion with cupric oxide, some sulphur dioxide, which may be combined by introducing a layer of lead peroxide (*Zeitschrift f. anal. Chemie*, 17, 1). Or lead chromate may be substituted for the cupric oxide. This would convert the sulphur into non-volatile lead sulphate. In the combustion of organic salts of the alkalis or earths, a portion of the carbon dioxide is retained by the base. To prevent this and to expel the  $\text{CO}_2$ , the substance in the boat is mixed with some potassium bichromate or chromic oxide (*Berichte* 13, 1641).

#### DETERMINATION OF NITROGEN.

In many instances, the presence of nitrogen is disclosed by the odor of burnt feathers when heat is applied to the compounds under examination. Many nitrogenous substances yield ammonia when heated with alkalis (best with soda-lime). A simple and very delicate test for the detection of nitrogen is the following: Heat the substance under examination in a small test tube with some sodium or potassium. When the substance is explosive, add dry soda. Cyanide of potash, accompanied by slight detonation, is the product. Treat the residue with water; to the filtrate add ferrous sulphate containing a ferric salt and a few drops of potassium hydrate, then apply heat and add an excess of hydrochloric acid. An undissolved, blue-colored precipitate (Prussian blue), or a bluish-green coloration, indicates the presence of nitrogen in the substance examined.

Nitrogen is determined, quantitatively, either by volume, by burning the substance and collecting the liberated, free nitrogen, or as ammonia, by igniting the substance with soda-lime. The first method is applicable with all substances, while the second can only be employed with the amide and cyanide compounds, not with those containing the nitro group.

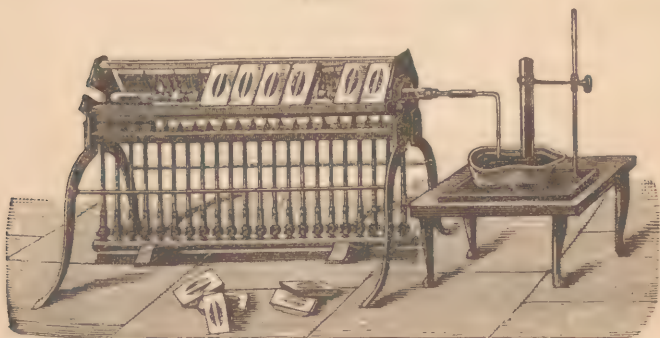
1. **Method of Dumas.**—In a glass tube fused shut at one end (length 70–80 cm.), place a layer (about 20 cm.) of dry, primary sodium carbonate or magnesite, then pure cupric oxide (6 cm.), afterwards the mixture of the substance with oxide, then again pure granular cupric oxide (20–30 cm.), and finally fill the tube with pure copper turnings (page 13) (about 20 cm.). In the open end of the tube is placed a rubber cork bearing a glass delivery tube, which extends into a mercury bath.

The back part of the combustion tube containing the carbonate is heated first; this causes the liberated carbon dioxide to expel the air from all parts of the apparatus. We can be certain of this by placing a test tube filled with potassium hydrate over the exit tube in the mercury trough. Complete absorption of the eliminated gases proves that air is no longer present. This done, a graduated cylinder filled with mercury is placed over the end of the exit tube and into the tube containing mercury is introduced, by means of



a pipette, several cubic centimetres of concentrated potassium hydrate. Proceed now with the combustion. First heat the metallic copper and the layer of cupric oxide in the anterior portion of the tube, and afterwards gradually approach the mixture. When the combustion is ended, again apply heat to another part of the sodium carbonate layer, to insure the removal of all the nitrogen from the tube and its entrance into the graduated tube. The potassium hydrate absorbs all the disengaged carbon dioxide, and only pure nitrogen remains in the graduated vessel. The latter is then placed in a large cylinder of water, allowed to stand a short time until the temperature is equalized, when the volume of gas is read and the temperature of the surrounding air and the barometer

FIG. 6.



height noted. With these data, the weight ( $G$ ) of the nitrogen volume, in grams, may be calculated from the formula—

$$G = \frac{V(h - w)}{760(1 + 0.00367t)} \times 0.0012562,$$

in which  $V$  represents the observed volume in cubic centimetres,  $h$  the barometric pressure, and  $w$  the tension of aqueous vapor at the temperature  $t$ . The number 0.0012562 is the weight, in grams, of 1 c. c. nitrogen at 0°C. and 760 mm. pressure.

The nitrogen determinations, as a general thing, are a little high in result, because it is almost impossible to drive out the air from the combustion tube, and the metallic copper sometimes contains H (page 13). It is, therefore, well to remove the air from the tube by a mercury air-pump (*Zeitschrift f. analyt. Chemie*, 17, 409).

Instead of collecting the disengaged nitrogen in an ordinary graduated glass tube, peculiar "azotometers" may be employed. Of these the apparatus of Schiff (*Berichte*, 13, 886), Zulkowsky (*ibid.* 1099), and Groves (*ibid.* 1341), may be recommended. Consult the *Zeitschrift für analyt. Chemie*, 17, 409, for a method in which carbon, hydrogen, and nitrogen are determined simultaneously.

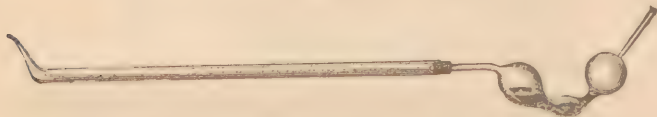
We can determine the nitrogen of nitro- and nitroso-compounds indirectly with



a titrated solution of stannous chloride. The latter converts the groups  $\text{NO}_2$  and  $\text{NO}$  into the amide group, with production of stannic chloride; the quantity of the latter is learned by the titration of the excess of stannous salt with an iodine solution. Method of Limpricht (*Berichte*, **11**, p. 40).

**2. Method of Will and Varrentrap.**—When most nitrogenous organic compounds (nitro-derivatives excepted) are ignited with alkalis, all the nitrogen is eliminated in the form of ammonia gas. The so-called soda-lime is best adapted for this decomposition; it is prepared by adding 2 parts lime hydrate to the aqueous solution of pure sodium hydrate (1 part), then evaporating the mixture and gently igniting it. Mix the weighed, finely pulverized substance with soda-lime (about 10 parts), place the mixture in a combustion tube about 30 cm. in length, and fill in with soda-lime. In the open end of the tube there is placed a rubber cork bearing a bulb apparatus (Fig. 7), in which there is dilute

FIG. 7.



hydrochloric acid. The anterior portion of the tube is first heated in the furnace, then that containing the mixture. To carry all the ammonia into the bulb, conduct air through the tube, after breaking off the point. The ammonium chloride in the hydrochloric acid is precipitated with platinic chloride, as ammonio-platinum chloride ( $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$ ), the precipitate ignited, and the residual Pt weighed; 1 atom of Pt corresponds to 2 molecules of  $\text{NH}_3$  or 2 atoms of nitrogen.

Generally, too little nitrogen is obtained by this method. A portion of the ammonia suffers decomposition. This is avoided by adding some sugar to the mixture of substance and soda-lime, and by not heating the tube too highly (*Zeitschrift*, **19**, 91). A more rapid volumetric method may be substituted for the gravimetric method in determining the ammonia. A definite volume of acid is placed in the bulb apparatus, and its excess after combustion ascertained by residual titration, employing fluorescein or methyl orange as indicator.

#### DETERMINATION OF THE HALOGENS.

Substances containing chlorine and bromine yield, when burned, a flame having a green-tinged border. The following reaction is exceedingly delicate. A little cupric oxide is placed on a platinum wire, ignited in a flame until it appears colorless, when a little of the substance under examination is put on the cupric oxide and this heated in the non-luminous gas flame. The latter is colored an intense greenish-blue in the presence of chlorine or bromine.

More decisive is to ignite the substance in a test tube with burnt lime, dissolve the mass in nitric acid, and then add silver nitrate.

The following *quantitative* methods for estimating halogens are in use:—

1. A difficultly fusible glass tube, closed at one end, and about 30 cm. in length, is partly filled with calcium oxide, then the mixture of the substance with lime, followed by a layer of calcium oxide. The latter should be free of chlorine. Heat the tube in a combustion furnace; after cooling shake its contents into dilute nitric acid, filter, add silver nitrate and weigh the precipitated silver haloid.

The decomposition is easier, if we substitute for lime a mixture of lime with  $\frac{1}{4}$  part sodium carbonate, or 1 part sodium carbonate, with 2 parts potassium nitrate, and in the case of difficultly volatilizable substances, a platinum or porcelain crucible heated over a gas lamp may be used (*Ann.* 195, 295 and 190, 40). With compounds containing iodine, iodic acid is apt to form; but after solution of the mass this may be reduced by sulphurous acid. The volumetric method of Volhardt (*Ann.* 190, 1) for estimating halogens by means of ammonium sulphocyanide may be employed instead of the customary gravimetric course.

The same decomposition can also be effected by ignition with ferric oxide (*Berichte* 10, 290).

2. *Method of Carius*.—The substance, weighed out in a small glass tube, is heated together with concentrated  $\text{HNO}_3$  and silver nitrate to  $150\text{--}300^\circ \text{C.}$ , in a sealed tube, and the quantity of the resulting silver haloid determined. The furnace of Babo (*Berichte* 13, 1219) is especially adapted for the heating of tubes.

3. In many instances, especially when the substances are soluble in water, the halogens may be separated by the action of sodium amalgam, and converted into salts, the quantity of which is determined in the filtered liquid.

#### DETERMINATION OF SULPHUR AND PHOSPHORUS.

The presence of sulphur is often shown by fusing the substance examined with potassium hydrate; potassium sulphide results, and produces a black stain of silver sulphide on a clean piece of silver. Heating the substance with metallic sodium is more accurate and always succeeds (even when sulphur is combined with oxygen): the aqueous filtrate is tested for sodium sulphide with sodium nitro-prusside.

In estimating sulphur and phosphorus ignite the weighed substance with a mixture of saltpetre and potassium carbonate; or, according to Carius, oxidize it by heating with nitric acid in a sealed tube. The resulting sulphuric and phosphoric acids are estimated by the usual methods.

Brügelmann employs a method not only applicable in the case of sulphur and phosphorus, but also adapted for the halogens. He burns the substances in an

open combustion tube in a current of oxygen, conducting the products through a layer of pure granular lime (or soda-lime), which is placed in the same tube, and is raised to a red heat. Later, the lime is dissolved in nitric acid, the halogens precipitated by silver nitrate, the sulphuric acid by barium chloride and the phosphoric acid (after removal of the excess of silver by HCl) by uranium acetate. Arsenic may be determined similarly (*Zeits. f. anal. Chemie*, 15, 1 and 16, 1). Sauer recommends collecting the sulphur dioxide, arising in the combustion of the substance, in hydrochloric acid containing bromine. (*Ibid* 12, 178.)

### DETERMINATION OF THE MOLECULAR FORMULA.

The elementary analysis affords the percentage composition of the analyzed substance. There remains, however, the deduction of the atomic-molecular formula.

We arrive at the simplest ratio in the number of elementary atoms contained in a compound, by dividing the percentage numbers by the respective atomic weights of the elements. Thus, the analysis of lactic acid gave the following percentage composition:—

Carbon.....	40.0	per cent.	
Hydrogen.....	6.6	"	
Oxygen.....	53.4	"	(by difference.)
	<u>100.0</u>		

Dividing these numbers by the corresponding weights (C = 12, H = 1, O = 16), the following quotients are obtained:—

$$\frac{40.0}{12} = 3.3 \quad \frac{6.6}{1} = 6.6 \quad \frac{53.4}{16} = 3.3$$

Therefore, the ratio of the number of atoms of C, H and O, in the lactic acid, is as 1 : 2 : 1. The simplest atomic formula, then, is  $\text{CH}_2\text{O}$ ; however, it remains undetermined what multiple of this formula expresses the true composition. Indeed, we are acquainted with different substances having the empirical formula  $\text{CH}_2\text{O}$ , for example, oxymethylene  $\text{CH}_2\text{O}$ , acetic acid  $\text{C}_2\text{H}_4\text{O}_2$ , lactic acid  $\text{C}_3\text{H}_6\text{O}_3$ , grape sugar  $\text{C}_6\text{H}_{12}\text{O}_6$ , etc. With compounds of complicated structure, the derivation of the simplest formula is, indeed, unreliable, because various formulas may be deduced from the percentage numbers by giving due regard to the possible sources of error in observation. The true molecular formula, therefore, can only be ascertained by some other means. Two courses of procedure are open to us. First, the study of the chemical reactions, and the derivatives of the substance under consideration, common to all cases. Second, the determination of the vapor density (compare Inorganic Chemistry, 4th Edition), especially adapted to volatile substances, and such as can be vaporized without undergoing decomposition.

The first method, of course, is rather complicated, and is usually executed by preparing derivatives, analyzing them and comparing their formulas with the supposed formula of the original compound. The problem becomes simpler when the substance is either a base or an acid. Then it is only necessary to prepare a salt, determine the quantity of metal combined with the acid, or of the mineral acid in union with the base, and from this calculate the equivalent formula. A few examples will serve to illustrate this.

Prepare the silver salt of lactic acid (the silver salts are easily obtained pure, and generally crystallize without water) and determine the quantity of silver in it. We find 54.8 per cent. Ag. As the atomic weight of silver = 107.7, the amount of the other constituent combined with one atom of Ag in silver lactate, may be calculated from the proportion—

$$54.8 : (100 - 54.8) :: 107.7 : x$$

$$x = 89.0.$$

Granting that lactic acid is monobasic, that in the silver salt one atom of H is replaced by silver, it follows that the molecular weight of the free (lactic) acid must =  $89 + 1 = 90$ . Consequently, the simplest empirical formula of the acid  $\text{CH}_2\text{O} = 30$  must be tripled. Hence, the molecular formula of the free acid is  $\text{C}_3\text{H}_6\text{O}_3 = 90$ :

$\text{C}_3 = 36$ .....	40.0
$\text{H}_6 = 6$ .....	6.7
$\text{O}_3 = 48$ .....	53.3

When we are studying a base, the platinum double salt is usually prepared. The constitution of these double salts is analogous to that of ammonio-platinum chloride— $\text{PtCl}_4 \cdot 2(\text{NH}_3\text{HCl})$ —the ammonia being replaced by the base. The quantity of Pt in the double salt is determined by ignition, and calculating the quantity of the constituent combined with one atom of Pt (198 parts). From the number found, subtract six atoms of Cl and two atoms of H, then divide by two; the result will be the equivalent or molecular weight of the base.

It is easier to deduce the molecular weight from the vapor density. According to the law of Avogadro, in equal volumes of all gases and vapors at like temperature and like pressure, we have an equal number of molecules. The molecular weights are, therefore, the same as the specific gravities. As the specific gravity is compared with  $\text{H} = 1$ , but the molecular weights with  $\text{H}_2 = 2$ , we ascertain the molecular weights by multiplying the specific gravity by two. Should the specific gravity be referred to air = 1,



then the molecular weight is equal to the specific gravity multiplied by 28.86 (since air is 14.43 times heavier than hydrogen).

	Molecular Weight.		Specific Gravity.	
Air.....	—	—	14.43	1
Hydrogen.....	H <sub>2</sub>	= 2	1	0.0693
Oxygen.....	O <sub>2</sub>	= 32	16	1.1060
Chlorine.....	Cl <sub>2</sub>	= 70.8	35.4	2.4550
Nitrogen.....	N <sub>2</sub>	= 28	14	0.970
Hydrogen Chloride...	HCl	= 36.4	18.2	1.262
Water.....	H <sub>2</sub> O	= 18	9	0.622
Ammonia.....	NH <sub>3</sub>	= 17	8.5	0.589
Methane.....	CH <sub>4</sub>	= 16	8	0.553
Ethane.....	C <sub>2</sub> H <sub>6</sub>	= 30	15	1.037
Pentane.....	C <sub>5</sub> H <sub>12</sub>	= 72	36	2.489
Ethylene.....	C <sub>2</sub> H <sub>4</sub>	= 28	14	0.964
Amylene.....	C <sub>8</sub> H <sub>10</sub>	= 70	35	2.430

The results arrived at by both methods—according to the chemical, by transpositions; according to the physical, by the vapor density—are always identical. Experience teaches this. If a deviation should occur, it is invariably in consequence of the substance suffering decomposition, or dissociation, in its conversion into vapor.

#### DETERMINATION OF THE VAPOR DENSITY.

Two essentially different principles underlie the methods employed in determining the vapor density. According to one, by weighing a vessel of known capacity filled with vapor, we ascertain the weight of the latter—method of Dumas. Or, in accordance with the other principle, a weighed quantity of substance is vaporized and the volume of the resulting vapor determined. In this case the vapor volume may be directly measured—methods of Gay-Lussac and A. W. Hofmann—or it may be calculated from the equivalent quantity of a liquid expelled by the vapor—displacement methods. The first three methods, of which a fuller description may be found in more extended text-books, are seldom employed at present in laboratories, because the recently published method of V. Meyer, characterized by simplicity in execution, affords sufficiently accurate results for all ordinary purposes. Consult *Berichte*, 15, 2777, upon the applicability of the various methods.

**Method of Victor Meyer.**—Vapor density determination by air displacement. According to this a weighed quantity of substance is vaporized in an enclosed space, and its equal volume of air, displaced by the vapor, measured. Fig. 8 represents the apparatus constructed for this purpose. It consists of a narrow glass tube about 600 mm. long, to which is fused the cylindrical vessel, *A*, of 100 c.cm. capacity. The upper, somewhat enlarged opening, *B*, is closed with a caoutchouc stopper. There is also a short capillary gas-delivery tube, *C*, intended to conduct out the dis-



placed air. It terminates in the water bath, *D*. The substance is weighed out in a small glass tube provided with a stopper, and vaporized in *A*. The escaping air is collected in the eudiometer, *E*. The vapor bath, used in heating, consists of a wide glass cylinder, *F*, whose lower, somewhat enlarged end, is closed and filled with a liquid of known boiling point. The liquid employed is determined by the substance under examination; its boiling point must be above that of the latter; some of the liquids in use are water ( $100^{\circ}$ ), xylene (about  $140^{\circ}$ ), aniline ( $184^{\circ}$ ), ethyl benzoate ( $213^{\circ}$ ), amyl benzoate ( $261^{\circ}$ ), and diphenylamine ( $310^{\circ}$ ); a lead bath is employed for higher temperatures (see *Berichte*, **11**, 1867 and 2253).

The method of operation is as follows: First clean and dry the apparatus, *A B*, by drawing air through it by means of a long, thin, glass tube, and, for safety, cover the bottom of *A* with ignited asbestos or pieces of fine platinum. Next place it in the heating cylinder, *F*, containing upwards of 200 c.cm. of the heating liquid, close *B* and dip the end of *C* into the water bath, *D*. With a lamp bring the contents of *F* to boiling; in this manner wholly encircling *A* with vapor, which condenses somewhat higher and flows regularly back. The air in *A* is thus heated, expands, and in part escapes from the side delivery tube through the water bath. The non-evolution of air bubbles indicates a *constant* temperature in *A B*, which is now prepared to receive the substance. The cork at *B* is rapidly removed, and the substance (0.05–0.1 gr.), weighed out in a small glass vessel, permitted to drop into *A*, the opening is again closed, and the end of the delivery tube, *C*, placed under the graduated tube filled with water. Below is described an improved method for the introduction of the substance. When the substance vaporizes it displaces an equal volume of air which collects in the graduated tube. The quantity of substance taken for each determination is always small, because it is desirable that the volume of its vapors

FIG. 8.



should not exceed  $\frac{1}{3}$  of the volume of  $A$ . As soon as bubbles are no longer emitted, the determination is finished. The graduated tube is stood to one side, the cork at  $B$  eased, to admit air and thus avoid the entrance of water when the apparatus cools. The volume of vapor formed is represented in the eudiometer by an equal volume of air, reduced to the temperature of the water bath and given air pressure. Read off its volume and note the temperature and barometric pressure.

The calculation of the vapor density,  $S$ , from the volume of gas found and the quantity of substance employed is simple. It equals the weight of the vapor,  $P$  (afforded by the weight of the substance employed), divided by the weight of an equal volume of air,  $P'$ —

$$S = \frac{P}{P'}.$$

1 c. cm. air at  $0^\circ$  and 760 mm. pressure weighs 0.001293 grams. The air volume found at the observed temperature is under the pressure  $H - w$ , in which  $H$  indicates the barometric pressure and  $w$  the tension of the aqueous vapor at temperature  $t$ . The weight then would be—

$$P' = 0.001293. \quad V. \frac{1}{1 + 0.00367 t} \cdot \frac{H - w}{760}$$

Consequently, the vapor density sought is—

$$S = \frac{P (1 + 0.00367 t.)}{0.001293. \quad V. H - w} \cdot \frac{760}{760}$$

V. Meyer's method affords results that are perfectly satisfactory *practically*, although not without some slight error in principle. Results from it, however, answer, because in deducing the molecular weight from the vapor density, relatively large numbers are considered and the little differences discarded. A greater inaccuracy may arise in the method in filling in the substances as described, because air is apt to enter the vessel. This may be avoided as follows (*Berichte*, 13, 1079): The end  $B$  is attached by a short rubber tube to a glass tube, lying horizontally, containing the tube holding the substance and closed by a rubber attachment. When constant temperature is attained in the apparatus, the substance is dropped into it by raising the horizontal tube, and then restoring it to its original position. Another method of introducing the substance is described in the *Berichte*, 13, 991. To test the decomposability of the substance at the temperature of the experiment, heat a small portion of it in a glass bulb provided with a long point (see *Berichte*, 14, 1466).

Substances boiling above  $300^\circ$  are heated in a lead-bath (*Berichte*, 11, 2255). Porcelain vessels are used when the temperature required is so high as to melt glass, and the heating is conducted in gas-ovens (*Berichte*, 12, 1112). Where air affects the substances in vapor form, the apparatus is filled with pure nitrogen. For modifications in methods of determining the density of gases, consult V. Meyer, *Berichte*, 13, 2019, and 15, 137, 1161 and 2771; Crafts, *Berichte*, 13, 851, 14, 356, and 16, 476. For air-baths and regulators, see L. Meyer, *Berichte*, 16, 1087.

II. Schwarz recommends the ordinary combustion tubes as substitutes for those of Meyer. The tubes, too, instead of being vertical, lie horizontally, and are heated in the common combustion furnace (*Berichte*, 16, 1051). Consult *Berichte*, 16, 1293, for a simple modification of Dumas' method, by Pawlewski.

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## CHEMICAL STRUCTURE OF THE CARBON COMPOUNDS.

The molecular weight of a given substance, and the absolute number of atoms contained in the latter, are ascertained by elementary analysis, and the study of the chemical transpositions, or by the determination of the vapor density. The problem of establishing the chemical formula of a compound would soon be solved, did not experience show that very often entirely different substances are possessed of the same molecular composition. *Isomerides* (from *ἰσομερής*, consisting of equal parts), is the name given these. In a more extended sense, isomerism includes all bodies of like percentage composition. When the isomerism depends upon a difference in molecular weight (p. 18), it is termed *polymerism*; a special case of the latter is the allotropy of the elements (see Inorganic Chemistry, 4th Ed.).

Real isomerism, *i. e.*, the phenomenon of bodies of like composition and like number of atoms, being different, is interpreted only by granting a different grouping or arrangement of the atoms in the molecule. That this, indeed, occurs, follows from the investigation of chemical reactions, as it is easy to split off from isomeric bodies entirely different atomic groups and atoms, or even to replace them by others. Hence, the atoms in such compounds are differently distributed or linked to one another. To investigate this different chemical union of the atoms, the *chemical constitution* of compounds—as an expression for their entire chemical deportment—is the task presented us. Since, however, the nature of chemical affinity and the manner of the union of atoms to molecules are absolutely unknown to us, the expression of chemical constitution can only be hypothetical—a mere formulation of the actually known regularities in the chemical transpositions of compounds.

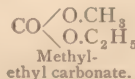
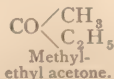
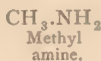
The various attempts to formulate the chemical constitution of compounds belong to the history of chemistry (p. 32). At present, the problem, especially in its relation to the derivatives of carbon, is, to a great extent, solved by the doctrine or theory of chemical structure. This is based upon the ideas of differences in valence in the elementary atoms, and upon their capability of combining by single affinity units (see Inorganic Chemistry).

Although the number of cases of isomerism is but limited in inorganic chemistry, and there being consequently but little importance attached to the presentation of structural formulas, the phe-

nomena of this kind are exceedingly abundant with the carbon compounds, so that constitutional or structural formulas, representing the entire chemical department, are absolutely necessary. Frequently, very complicated relations occur, yet the structure of all investigated carbon derivatives may be deduced from the following principles:—

1. The carbon atoms, in their hydrogen combinations, are constantly quadrivalent. The position of carbon in the periodic system gives expression to this fact. The only derivative in which carbon apparently figures as a bivalent element is carbon monoxide CO (see below).

2. The four affinity units are, as generally represented, equal and similar, *i. e.*, no differences can be discovered in them when they form compounds. If these four affinities be attached to different elements or groups, the order of their combination is entirely immaterial. The compounds—

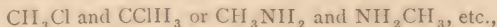


are known but in one modification each; their isomerides have never been prepared.

3. The carbon atoms can unite in a chain-like series, by combining with each other by one or more units. This they can do, also, with other elementary atoms.

These principles express the relations really known at present. All investigated compounds prove carbon to be quadrivalent. Carbon monoxide CO is not a contradiction, as valence is a function of the atoms (compare *Inorganic Chemistry*, 4th Ed.), and its existence is effected in the same way by the nature of oxygen, as by carbon; we can, with equal correctness, represent O in CO as quadrivalent and C as bivalent. Because CO does exist, it in no manner follows that carbon can figure as a dyad in the hydrogen derivatives. Repeated efforts to prepare compounds containing bivalent carbon were unsuccessful (page 28).

The equi-valence of the four carbon affinities, in the sense above illustrated, has likewise been positively confirmed. By the early type or substitution theory, it appeared possible that compounds like

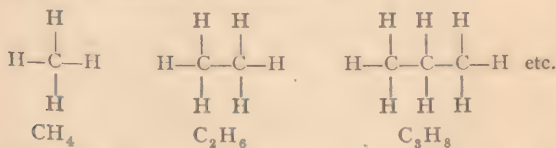


were isomeric. All experiments instituted proved that the succession of substitution or the replacement of the substituting atoms again were without effect; identical bodies resulted in all analogous cases.

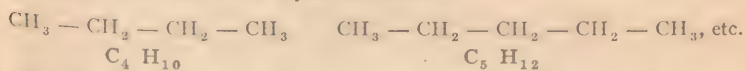
It may be added, in regard to the capability of union of the carbon atoms with each other and with other elements, that all the imaginable combinations are really not possible. Certain groupings can in no way be realized, and the union of two atoms is very often influenced by the atoms present with them in the molecule. The related phenomena, which are of such great interest as regards the constitution, will be developed later, in special cases.



The different manner, in the linking of the carbon atoms, shows itself most plainly in their hydrogen compounds—in the so-called hydrocarbons. By removing one atom of hydrogen from the simplest hydrocarbon, methane  $\text{CH}_4$ , the remaining univalent group  $\text{CH}_3$ , can combine with another, yielding  $\text{CH}_3-\text{CH}_3$ , or  $\text{C}_2\text{H}_6$ , ethane or dimethyl. Here, again, a hydrogen atom may be replaced by the group  $\text{CH}_3$ , resulting in the compound  $\text{CH}_3-\text{CH}_2-\text{CH}_3$  propane. The structure of these derivatives may be more clearly represented graphically:—

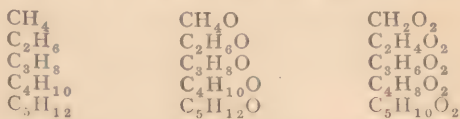


By continuing this chain-like union of the carbon atoms, there arises an entire series of hydrocarbons—



having the common formula  $\text{C}_n \text{H}_{2n+2}$ , in which each member differs from the one immediately preceding and the one following, by  $\text{CH}_2$ .

The compounds constituting such a series are said to be *homologous*. In addition to the hydrocarbons forming such a series, many others exist, *e. g.*, the monohydric alcohols and monobasic acids:—



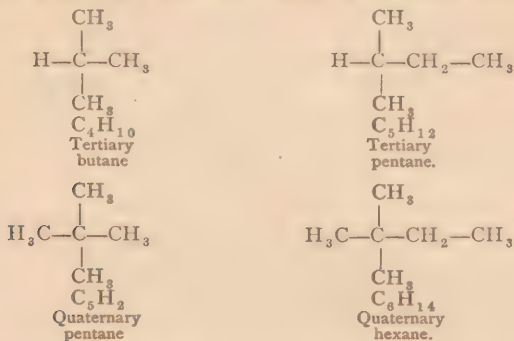
The compounds belonging to such an homologous series, because of their similarity in chemical structure, exhibit great analogy in their entire chemical character.

The manner of union just considered, that of a simple, open chain, is designated *normal structure*. In this we distinguish intermediate and terminal carbon atoms; the first are connected with two other carbon atoms and have two valence units which may be saturated by two hydrogen atoms (or other elements). The terminal carbon atoms of the chain are combined with three hydrogen atoms. Usually, the normal structure may be expressed by the following formulas:—





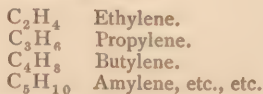
Carbon atoms can unite with even three or four other carbon atoms, then *tertiary* or *quaternary* union or structure arises:—



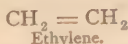
This varying union of the carbon atoms explains the numberless isomerides possible for the higher series. This will be especially observed in case of the hydrocarbons.

In all the structural cases introduced here, the two carbon atoms are in simple combination with each other. The number of valence units (hydrogen atoms) with which the carbon nuclei, consisting of  $n$  atoms, can directly combine equals  $2n + 2$  (p. 25). This cannot be exceeded without the consequent destruction of the carbon nucleus. Therefore, compounds constituted according to the general formula  $\text{C}_n\text{X}_{2n+2}$  (in which X represents the valences directly joined to C), are termed *saturated* compounds or *paraffins*.

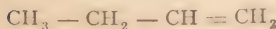
Besides the hydrocarbons  $\text{C}_n\text{H}_{2n+2}$ , there exists another homologous series (p. 25) of the form  $\text{C}_n\text{H}_{2n}$ :—



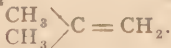
Their existence is accounted for by assuming that in them the carbon atoms are united by two valences—a *double* or *bivalent* union. The following structural formulas indicate this:—



For the formula  $\text{C}_4\text{H}_8$ , three structures are possible:—

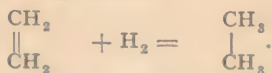


and



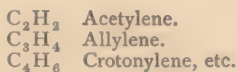
As only a simple union is required for the linking of the carbon atoms, such compounds as the last are capable of saturating two

valence units; they are, therefore, termed *unsaturated* compounds. By the addition of two hydrogen atoms, they pass into  $C_nH_{2n+2}$ . The double changes to single union:—



The acceptance of this double union of the carbon atoms in no manner indicates (as sometimes erroneously supposed) a closer, stronger combination. It has long been known, that the unsaturated compounds could be much more readily broken up than the saturated; and that they possess, too, a greater specific volume; hence, the double union is less intimate than the simple. (Compare 1st Ed. of this book, p. 40.) The use of the double lines represents the fact that only two directly combined carbon atoms are capable of saturation (p. 27).

A third series of hydrocarbons arises when a triple union of two carbon atoms occurs. Their composition corresponds to the common formula  $C_nH_{2n-2}$ :—

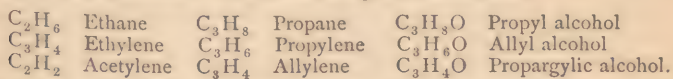


Their structural formulas are—

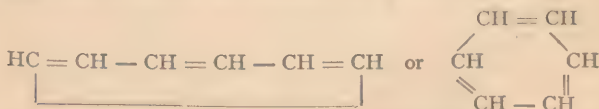


We can view these as unsaturated hydrocarbons of the second degree. They are capable of combining directly with two and four valences, passing into the compounds  $C_nH_{2n}$  or  $C_nH_{2n+2}$ .

Compounds containing a like number of carbon atoms, with a gradually decreasing number of hydrogen atoms, are designated *isologous compounds*. The following are examples:—

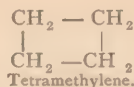
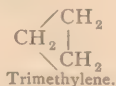


Finally, there is a large series of carbon compounds bearing the name *aromatic*. They all originate from a nucleus composed of six carbon atoms. Benzene  $C_6H_6$  represents their simplest combination. The simplest structure of this nucleus is probably one in which the six carbon atoms form a closed ring, with alternating single and double union, as represented by the following:—



The innumerable aromatic or benzene compounds resulting from the replacement of H in benzene by other atoms or groups, constitute a distinct class.

The ring-shaped compounds trimethylene  $C_3H_6$  and tetramethylene  $C_4H_8$ , recently described, are forerunners of the stable, closed benzene ring:—



By the replacement of hydrogen in these, there is likewise derived a series of compounds.

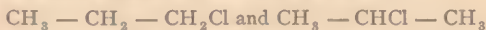
Formerly, another view prevailed relative to the unsaturated carbon compounds. It was assumed that bivalent carbon atoms could occur in the hydrogen compounds, just as well as in carbon monoxide. The other two affinities remained unsaturated or free. This view would allow the existence of innumerable isomeric derivatives. Thus two bodies  $CH_2 = CH_2$  and  $CH_3 - \overset{''}{C}H$  could correspond to the formula  $C_2H_4$ , but only the first really exists. In addition to the true propylene  $CH_3 - CH = CH_2$ , two other bodies,  $CH_3 - CH_2 - \overset{''}{C}H$  and  $CH_3 - \overset{''}{C} - CH_3$  could correspond to the formula  $C_3H_6$ . The preparation of such isomerides has been fruitless. The compound  $CH_2$ , methylene (see this), cannot be made. In the case of all sufficiently well-studied unsaturated compounds, it is established that the two free valences *invariably belong to two different carbon atoms*. By adding two atoms of chlorine to ethylene  $CH_2 = CH_2$ , there arises the compound  $CH_2Cl - CH_2Cl$ ; the isomeride  $CH_3\overset{''}{C}H$  should yield  $CH_3 - CHCl_2$ . Inversely, we get ethylene  $CH_2 = CH_2$ , from its chloride  $CH_2Cl - CH_2Cl$ , while the isomeric, so-called ethylidene  $CH_3\overset{''}{C}H$  cannot be obtained from ethylidene chloride  $CH_3 - CHCl_2$ . If really, as above supposed, the free affinities of the two carbon atoms are combined with each other—if double union occur—it cannot be asserted with certainty, and it is entirely irrelevant, as we possess no representation as to the nature of the union. It is doubtless certain that the possibility of the so-called free valence of a carbon atom is influenced by the free valence of another atom, which is in *direct* union with the first. It is very likely there exists  $CH_3 - CH_2 - CH_2$  (propylene), but not the forms  $CH_3 - CH_2 - \overset{''}{C}H$  or  $CH_3 - \overset{''}{C} - CH_3$ . This knowledge, answering the actual facts, considerably limits the number of possible isomerides, and finds expression in the supposition of the constant tetravalence of carbon. So long as convincing reasons are not present, we must refrain from introducing a new, fundamental, and far reaching hypothesis, which would remove the existing regularities.

In the preceding pages we have discussed the different ways in which the carbon atoms are bound to each other in their hydrogen derivatives. We meet these in all other carbon compounds that may be regarded as derivatives of the hydrocarbons, resulting from the replacement of hydrogen by other elements or groups.

Since all the facts go to prove that the four valences of the carbon atom are similar (p. 24), isomerisms in similar carbon nuclei can take place only when the entering elements or groups attach themselves to carbon atoms with different functions; or, as ordinarily

expressed, when they occupy different *chemical positions*. The following examples serve to illustrate :—

According to the formula  $C_2H_5Cl$ , there can be but one body of the structure  $CH_3 - CH_2Cl$ , because, in the original substance  $CH_3 - CH_3$  dimethyl, both carbon atoms act alike. On the other hand, two isomeric bodies of the structure—



correspond to the formula  $C_3H_7Cl$ , because, in propane  $CH_3 - CH_2 - CH_3$  from which they originate, the carbon atoms are not similarly united, consequently, the entering halogen atoms can occupy relatively different positions. Thus, too, four isomerides correspond to the formula  $C_4H_9Cl$ , two springing from normal butane  $CH_3 - CH_2 - CH_2 - CH_3$ , two from isobutane—



The number of isomerides is further increased by the entrance of two or several similar or dissimilar atoms or groups. For the formula  $C_2H_4Cl_2$  we have two isomerides  $CH_2Cl - CH_2Cl$  and  $CH_3 - CHCl_2$ .

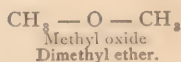
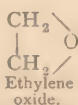
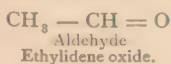
For the formula  $C_3H_6Cl_2$  four structural cases are possible :—



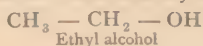
All other possible isomerides are derived in the same manner. The nature of the atoms or groups entering is immaterial as far as the isomeric relations (p. 24) are concerned.

Compounds obtained from the hydrogen derivatives by the replacement of hydrogen by halogens or the nitro group  $NO_2$  are usually designated *substitution products*; generally, they retain the chemical character of the parent substance. In a broader sense, one can consider all carbon compounds as substitution derivatives of the hydrocarbons or of methane  $CH_4$ .

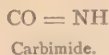
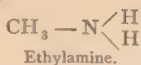
Two bivalent elements like S and O can unite with C with either one or two valences. In the first case, they may be combined with one or two carbon atoms—



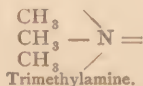
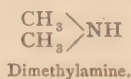
If the bivalent element unite with but one affinity to carbon, the other must be saturated by some other element :—



Likewise, the trivalent elements, like nitrogen and phosphorus, may unite with carbon with all or with one affinity—either with one carbon atom—

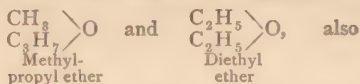


or with two or three carbon atoms—



In this way two or more carbon atoms may be united to a molecule through the agency of an element of higher valence.

Those isomeric bodies (of like composition) containing several but different carbon groups, held in combination by an atom of higher valence, are termed *metameric*. Examples are—



These can be resolved by various reactions into their component carbon groups (or their derivatives), and inversely be synthesized from these groups or their derivatives.

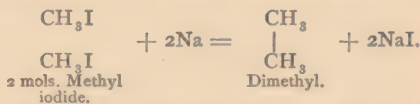
*Law of Conjugate Atomic Numbers.*—In every carbon compound, the sum of the elements of uneven valence (of the monads and triads), like H, Cl, Br, and I, and N, P, As, is an even number. Thus, in cyanuric acid  $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$ , the sum of the hydrogen and nitrogen atoms = 6; in ammonium trichloracetate  $\text{C}_2\text{Cl}_3(\text{NH}_4)\text{O}_2$ , the sum of the atoms of Cl, N and H = 8. This law, established empirically at first, and of importance in the deduction of chemical formulas, finds, at present, as observed in preceding lines, a simple explanation in the quadrivalent nature of carbon and the property of the elements to unite themselves by single affinities.

**Radicals and Formulas.**—Radicals or residues are atomic groups remaining after the removal of one or more atoms from saturated molecules. Ordinarily, *radicals* are groups containing carbon, while all others, like OH, SH,  $\text{NH}_2$ ,  $\text{NO}_2$ , are *residues* or groups. By the successive removal of hydrogen from the hydrocarbons of the formula  $\text{C}_n\text{H}_{2n+2}$ , radicals of different, increasing valence result. These may combine with other elements or groups until the form  $\text{C}_n\text{H}_{2n+2}$  is attained—

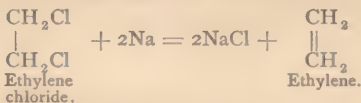


RADICALS.	Molecules	$\text{CH}_4$ Methane	$\text{C}_2\text{H}_6$ Ethane	$\text{C}_3\text{H}_8$ Propane	$\text{C}_4\text{H}_{10}$ Butane
	univalent	$\text{CH}_3$ Methyl	$\text{C}_2\text{H}_5$ Ethyl	$\text{C}_3\text{H}_7$ Propyl	$\text{C}_4\text{H}_9$ Butyl
	bivalent	$\text{CH}_2$ Methylene	$\text{C}_2\text{H}_4$ Ethylene	$\text{C}_3\text{H}_6$ Propylene	$\text{C}_4\text{H}_8$ Butylene
	trivalent	$\text{CH}$ Methine	$\text{C}_2\text{H}_3$ Vinyl	$\text{C}_3\text{H}_5$ Glyceryl	$\text{C}_4\text{H}_7$ Crotonyl
	quadrivalent	$\text{C}$ Carbon	$\text{C}_2\text{H}_2$ Acetylene	$\text{C}_3\text{H}_4$ Allylene	$\text{C}_4\text{H}_6$ Crotonylene.

It may be observed from the preceding pages, that radicals are not capable of existing free. When the univalent radicals separate from their compounds, they double themselves:—

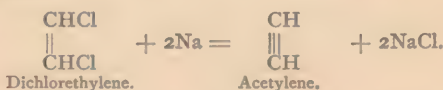


The bivalent and quadrivalent radicals can only be isolated from their compounds when the affinities that are liberated belong to two adjacent carbon atoms—that is, those mutually uniting each other—



The radical  $\text{CH}_3 - \text{CH} =$  cannot be isolated from  $\text{CH}_3 - \text{CHCl}_2$  (comp. p. 28).

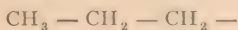
As in the examples just given, acetylene may be obtained from dichlorethylene—



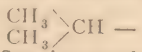
The acceptance of radicals leads to a special nomenclature of the compounds. *Monochlorethane*  $\text{C}_2\text{H}_5\text{Cl}$ , derived by substitution from the molecule of ethane  $\text{C}_2\text{H}_6$ , may be viewed as a compound of the group ethyl with chlorine, hence, called *Ethylchloride*.  $\text{CH}_2\text{Cl}_2$  is called *dichlormethane* or *methylene chloride*;  $\text{C}_2\text{H}_5\text{NH}_2$  is known as *amidoethane* or *ethylamine*, etc. For this reason it is customary to ascribe especial names to the simpler and more frequently occurring radicals or atomic groups (see above). *Alcoholic radicals* or *alkyls* is the name applied to the univalent radicals  $\text{C}_n\text{H}_{2n+1}$  from their most important compounds—the alcohols  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . Those groups that are bivalent are called *alkylens* etc.

The univalent radicals are again distinguished as *primary*, *second-*

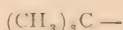
ary and tertiary, according as the unsaturated carbon atom is attached to one, two or three carbon atoms—



Primary propyl.



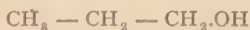
Secondary propyl.



Tertiary butyl.

These correspond to the primary, secondary and tertiary alcohols (see these).

*Structural formulas* are those indicating the complete grouping of all the atoms:—



Primary propyl alcohol



Secondary, or Isopropyl alcohol.

These are a representation of the whole chemical deportment of a given compound. The rational or *constitutional formulas* only indicate the union of individual atoms—such as are especially characteristic of the compound. Thus, the formula  $\text{C}_3\text{H}_7.\text{OH}$  indicates that the body is an alcohol; has properties common to all alcohols; it leaves undetermined, however, whether it is a primary or a secondary alcohol. For simplicity we employ such formulas and grant special names to the isomeric radicals. The *empiric* or *unitary* formula  $\text{C}_3\text{H}_7(\text{O})$  affords no hint as to the character of the compound, since it belongs to an entire series of bodies that are isomeric, yet wholly different.

#### EARLY THEORIES RELATING TO THE CONSTITUTION OF THE CARBON COMPOUNDS.

The opinion that the cause of chemical affinity resided in electrical forces, came to light in the commencement of this century, when the remarkable decompositions of chemical bodies were discovered, through the agency of the electric current. It was assumed that the elementary atoms possessed different electrical polarities, and the elements were arranged in a series according to their electrical deportment. Chemical union depended on the obliteration of different electricities. The *dualistic* idea of the constitution of compounds was a necessary consequence of this hypothesis. According to it, every chemical compound was composed of two groups, electrically different, and these were further made up of two different groups or elements. Thus, salts were viewed as combinations of electro-positive bases (metallic oxides), with electro-negative acids (acid anhydrides), and these, in turn, were held to be binary compounds of oxygen with metals and metalloids. (See *Inorganic Chemistry*, 4th Edition.) With this basis, there was constructed the *electro-chemical, dualistic theory of Berzelius*. This prevailed almost exclusively in Germany, until about 1860.

The principles predominating in inorganic chemistry were also applied to organic substances. It was thought that in the latter complex groups (radicals) pre-existed, and played the same rôle that the elements did in mineral matter. Organic chemistry was defined as the chemistry of the compound radicals (Liebig, 1832), and led to the *chemical radical theory*, which flourished in Germany simultaneously with the *electro-chemical* theory. According to this view, the object of organic chemistry was the investigation and isolation of radicals, in the sense of the dualistic idea, as the more intimate components of the organic compounds, and by this means they thought to explain the constitution of the latter.

In the meantime, about 1830, France contributed facts not in harmony with the electro-chemical, dualistic theory. It had been found that the hydrogen

in organic compounds, could be replaced (substituted) by chlorine and bromine, without the character of the compounds, to all appearance, suffering very essentially. To the electro-negative halogens was ascribed a chemical function similar to electro-positive hydrogen. This showed the electro-chemical hypothesis to be erroneous. The dualistic idea was superseded by a *unitary* theory. Putting aside all the primitive speculations on the nature of chemical affinity, the chemical compounds began to be looked upon as constituted in accordance with definite mechanical ground-forms—*types*—in which the individual elements could be replaced by others (early type theory of Dumas, nucleus theory of Laurent). At the same time the dualistic view on the pre-existence of radicals was refuted. The correct establishment of the ideas, *equivalent, atom and molecule* (Laurent and Gerhardt), are an important consequence of the typical unitary idea of chemical compounds. By means of this, was laid a correct foundation for further generalization. The molecule having been determined a chemical unit, the study of the grouping of atoms in the molecule became possible, and chemical constitution could again be more closely examined. The investigation of the reactions of double decomposition, whereby single atomic groups (radicals or residues) were preserved and could be exchanged (Gerhardt); the important discoveries of the amines or substituted ammonias by Würtz (1849), and Hofmann (1850); the epoch-making researches of Williamson, upon the composition of ethers, and the discovery of acid-forming oxides by Gerhardt—these all contributed to the announcement of the *type theory of Gerhardt* (1853), which is nothing more than an amalgamation of the early type or substitution theory of Dumas and Laurent with the radical theory of Berzelius and Liebig. The molecule is its basis—then follows a more extended grouping of the atoms in the molecule. The conception of radicals became different. They were no longer held as atomic groups that could be isolated and comparable with elements, but as molecular residues which remained unaltered in certain reactions.

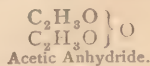
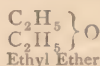
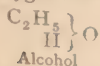
Comparing the carbon compounds with the simplest inorganic derivatives, Gerhardt referred them to the following principal ground-forms or types:—



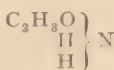
From these they could be produced by substituting the compound radicals for hydrogen atoms. All compounds that could be viewed as consisting of two directly combined groups were referred to the hydrogen and hydrogen chloride type, *e. g.*:—



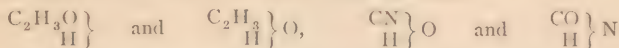
It is customary to refer all those bodies derivable from water by the replacement of hydrogen to the water type; *i. e.*, those in which two groups are united by oxygen:—



The compounds containing three groups united by nitrogen are considered ammonia derivatives:—



These types no longer possessed their early restricted meaning. Sometimes one body was referred to different types, according to the transpositions intended to be expressed by the formula. Thus aldehyde was referred to the hydrogen or water type; cyanic acid to the water or ammonia type:—

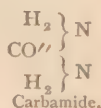
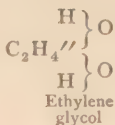
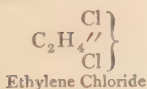


The development of the idea of polyatomic radicals, the knowledge that the hydrogen of carbon radicals could be replaced by the groups OH and NH<sub>2</sub>, etc., contributed to the further establishment of *multiple* and *mixed* types:—

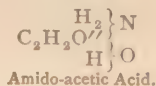
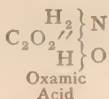
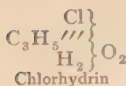
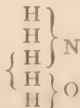
*Compound Types:—*



*e. g.:*—



*Mixed Types:—*



The manner of arrangement finding expression in these multiple and mixed types was this: two or more groups were united into one whole—a molecule—by the univalent radicals. Upon comparing these typical with the structural formulas employed at present, we observe that the first constitute the transitional state from the empirical to the unitary formulas of the present day. The latter aim to express the perfect grouping of the atoms in the molecule. By granting a particular function to the atoms—their atomicity or valence—Kekulé (1858) indicated the *idea of types*; the existence and combining valence of radicals was explained by the tetravalence of the carbon atoms, and their tendency to mutually combine with each other, according to definite affinity units (Kekulé and Couper). The type theory, consequently, is not, as sometimes declared, laid aside as erroneous; but it has only found generalization and amplification in a broader principle—just as the present structural theory will, at some future time, find wider importance in a more general hypothesis which encompasses the nature of chemical affinity.

## PHYSICAL PROPERTIES OF THE CARBON COMPOUNDS.

Usually we can foresee that the physical, as well as the chemical, properties of the derivatives of carbon must be conditioned by their composition and constitution. Such a regular connection, however, has been as yet only approximately established for a few



properties. Those meriting consideration here, serving, therefore, chiefly for the external characterization of carbon derivatives, are the specific gravity in the gaseous and liquid condition; the melting and boiling temperatures and the behavior towards light.

#### SPECIFIC GRAVITY.

By this term is understood the relation of the absolute weights of equal volumes of bodies, in which case we take as conventional units of comparison, water for solids and liquids, and air or hydrogen for gaseous bodies (see p. 19).

For the latter, as we have already seen, the ratio of the specific gravity (gas density) to the chemical composition is very simple. Since, according to Avogadro's law, an equal number of molecules are present in equal volumes, the gas densities stand in the same ratio as the molecular weights. Therefore, the *specific volume*, *i. e.*, the quotient of the molecular weight and specific gravity, is a constant quantity for all gases (at equal pressure and temperature). The relations are different in the cases of liquid and solid bodies. Since in the solid and liquid states the molecules are considerably nearer each other than when in the gas condition, the specific gravities cannot be, as with gases, proportional to the molecular weight, and are also modified by the size of the molecules and their distance from each other. The size and distance are unknown to us; the latter increases, too, with the temperature, therefore, the theoretical groundwork for deduction of specific gravities is far removed from us. However, some regularities have been empirically established for the specific gravity of *liquid* bodies. These appear, according to H. Kopp, upon comparing the specific volumes at the boiling points of the liquids, at which the tension of the vapors is the same for all; one can also assume that the relations of the volumes to the molecular weights will be more regular at such points.

In determining the specific gravity, a small bottle—a pyknometer—is used. Its contracted portion is provided with a mark; more complicated apparatus is employed where greater accuracy is sought (*Annalen* 203, 4). Descriptions of modified pyknometers will be found in Pogg., *Annalen* 19, 378. To get comparable numbers, it is recommended to make all determinations at a temperature of 20° C., and refer these to water at 4°, and a vacuum. Letting *m* represent the weight of substance, *v* that of an equal volume of water at 20°, then the specific gravity at 20° referred to water at 4°, and a vacuum (with an accuracy of four decimals), may be ascertained by the following equation (*Annalen* 203, 9):—

$$d \frac{20}{4} = \frac{m \cdot 0.99707}{v} + 0.0012.$$

To find the specific volumes at the boiling temperature, the specific gravity at any temperature, the coefficient of expansion and the boiling point must be ascertained; with these data the specific gravity at the boiling point is calculated, and



by dividing the molecular weight by this there results the specific or molecular volume. Kopp's dilatometer (*Annalen* 94, 257, compare Thorpe, *Journal Chem. Soc.* 1880, 141, and Weger, *Annalen* 221, 64), is employed in obtaining the expansion of liquids. For another method of getting the specific gravity at the boiling point, consult R. Schiff, *Annalen*, 220, 78, and *Berichte*, 14, 2761.

H. Kopp ascertained the following relations existing between the composition of carbon compounds and their molecular volumes at the boiling temperature:—

1. Isomeric compounds possess approximately like specific volumes. 2. In homologous compounds the difference,  $\text{CH}_2$ , corresponds to a difference of 22\* in specific volume, for example—

		Molecular Weight.	Specific Volume.	Difference.
Formic Acid.....	$\text{CH}_2\text{O}_2$	46	42	} 22
Acetic Acid.....	$\text{C}_2\text{H}_4\text{O}_2$	60	64	
Propionic Acid.....	$\text{C}_3\text{H}_6\text{O}_2$	74	86	} 22
Butyric Acid.....	$\text{C}_4\text{H}_8\text{O}_2$	88	108	

3. The replacement of a carbon atom by two hydrogen atoms, does not cause any alteration in specific volume *e. g.*,

		Molecular Weight.	Specific Volume.
Cymene.....	$\text{C}_{10}\text{H}_{14}$	134	187
Octane.....	$\text{C}_8\text{H}_{18}$	114	187

We perceive the molecular volumes depend on the number of different atoms contained in the molecules. Since the specific volume of the group  $\text{CH}_2$  equals 22, the specific volume of one atom of C, however, being equal to two hydrogen atoms, it follows that the specific volume of a carbon atom (its atomic volume) is 11, and that of one hydrogen atom 5.5.

In a similar manner two different atomic volumes may be deduced for oxygen. If oxygen be in union with both affinities to one carbon atom (CO), its atomic volume would equal 12.2; but if it be combined with two different atoms (as in  $(\text{CH}_3)_2\text{O}$  and  $\text{CH}_3\text{OH}$ ) its atomic volume would be 7.8. Hence, the specific volume of a compound of the formula  $\text{C}_a\text{H}_b\text{O}_c\text{O}'_d$  (O represents intra- and O' extra-radical oxygen) may be calculated according to the equation—

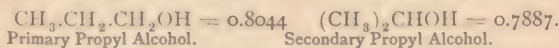
$$\text{Specific Volume} = 11 \cdot a + 5.5 \cdot b + 12.2 \cdot c + 7.8 \cdot d.$$

The other elements exhibit similar definite specific volumes in their compounds, *e. g.*, chlorine = 22.8, bromine = 27.8, iodine = 37.5. Sulphur, like oxygen, has two values: the atomic volume of the intra-radical (CS) equals 28.6; that of the extra-radical, 22.6. In ammonia and its derivatives, nitrogen has the specific volume 2.3, in the CN group 17, in  $\text{NO}_2$ , 8.6.

\* Recent investigations indicate a difference, varying from 19–24 at the boiling temperature; at the melting temperature it is 17.8 (*Ber.* 15, 1726).

With such data the specific volumes, and, of course, the specific gravities, can be obtained with approximate accuracy. The molecular volume equals the sum of the atomic volumes. Since the specific volumes of oxygen, sulphur and nitrogen vary according to their different compounds, the specific volumes found would afford a key to the structure of the derivatives.

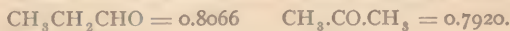
The regularities cited above were obtained at a time when isomeric relations, deduced by a different linking of the carbon atoms, found no consideration. The latest investigations\* prove that isomeric bodies do not at all always possess equal molecular volumes. The different manner in which the carbon atoms are united exercises an influence upon the molecular volume or the specific gravity, just as observed in the case of the various combinations of oxygen and nitrogen. In general bodies possessing normal structure of the carbon atoms exhibit a higher specific gravity, hence, a smaller molecular volume, than those of tertiary or quaternary structure (see p. 26). For example, the specific gravity of normal butyl alcohol  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$  equals 0.8099, that of iso-butyl alcohol  $(\text{CH}_3)_2 \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$  0.8062. Similarly, the derivatives of primary radicals (see p. 31) possess higher specific gravity than those of the secondary or tertiary.



Primary Propyl Alcohol.

Secondary Propyl Alcohol.

Commonly, substitution upon a terminal carbon atom appears to bring about greater density than when an intermediate C atom has been acted upon:—



Propyl Aldehyde.

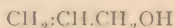
Acetone.

The influence of double and triple union of carbon atoms is worthy of consideration. The unsaturated compounds exhibit a higher specific gravity than the corresponding saturated:—



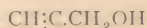
Propyl Alcohol

Sp. gr. 0.8044



Allyl Alcohol

0.8540



Propargylic Alcohol.

0.9715

The molecular volumes of the unsaturated compounds of the fatty series range, according to Buff, 1.5–3.0 higher than deduced by Kopp; later research makes the difference about 4. (Compare *Annalen*, 214, 121, 220, 291, and 221, 102). Therefore, the carbon atoms united by two affinities like the oxygen atoms combined doubly with carbon, must occupy a greater volume. In accord with this, the unsaturated compounds possess higher heat of combustion (*Annalen*, 211, 125, 220, 320), and exercise greater light refracting power (see p. 40). On the other hand, the derivatives of benzene do not have as high a specific volume as the unsaturated derivatives, hence in them the mutual union of the C atoms appears not to occur in an analogous manner (see *Annalen*, 214, 130, 220, 303 and 221, 107).

## MELTING POINTS—BOILING POINTS.

Every pure carbon compound, if at all fusible or volatile, exhibits a definite melting and boiling temperature. It is customary to determine these for the characterization of the substance.

**Boiling Points.** These are determined in a so-called boiling flask, *i. e.*, a small flask with wide neck, and provided on the side

\* Lossen, *Annalen* 214, 81; Zander, *Annalen* 214, 138; Thorpe, *Journ. Chem. Soc.* 1881, 141 and 327; Staedel, *Berichte* 15, 2559; R. Schiff, *Annalen* 220, 113 and 278; Weger, *Annalen* 221, 61.

with an exit tube. The thermometer is fixed in the opening of the neck by means of a cork. It should not be allowed to dip into the liquid; it must only be surrounded by the vapors.

In accurate determinations it is necessary to apply corrections to the indicated temperatures. If a thermometer is not wholly immersed in vapor, but as ordinarily happens, is partly extended into the air beyond the distillation vessel, the external mercury column will not be heated the same as that on the interior, hence the recorded temperature will be less than the real. The necessary correction will be reached with sufficient accuracy by adding to the observed temperature the quantity  $n(T - t)$ , 0.000154. Here  $n$  indicates the length of the mercurial column without the vessel, in degrees of the thermometer,  $T$  the observed temperature,  $t$  the medium temperature of the air about the external column of mercury (this is approximately ascertained by holding a second thermometer about the middle of the exposed part); 0.000145 is the apparent coefficient of expansion of mercury in glass. The correction is best avoided by having the entire mercurial column played upon by the vapors of the liquid. Pawlewski has presented a simple device to effect this (*Berichte*, 14, 88). It is also applicable in cases where but slight quantities of liquid are employed.

If the barometric column did not indicate a normal pressure of 760 mm. during the distillation a second correction in the observed boiling temperature is necessitated. This is ordinarily accomplished by either adding to or deducting from the observed temperature 0.1° C. for a difference of every 2.7 mm. between the observed and normal barometric height (760 mm.). This correction is, however, very inaccurate, because the "specific remission" for each compound at different pressures is very different (*Berichte*, 16, 2476). To avoid this correction it is advisable to reduce the pressure in the apparatus to the normal. The pressure regulators of Bunte (*Ann.*, 168, 139) and Lothar Meyer (*Ann.*, 195, 218; *Berichte*, 13, 839) are adapted to this purpose.

Liquids of different boiling points are separated by *fractional distillation*, an operation performed in almost every distillation. The portions passing over between definite temperature intervals (from 1-10°, etc.) are caught apart and subjected to repeated distillation, the portions boiling alike being united. To attain a more rapid separation of the rising vapors, these should be passed through a vertical tube. In this the vapors of the higher boiling compound will be condensed and flow back, as in the apparatus employed in the rectification of spirit. To this end there is placed on the boiling flask a so-called *fractional tube* of Würtz. Excellent modifications of this by Linnemann and Le Bel are described in *Annalen*, 160, 195, and *Berichte*, 7, 1085. It is often required to perform the distillation in *vacuo*; and this is best effected by exhausting the boiling chamber. An apparatus answering this purpose is mentioned in *Berichte*, 9, 1870. A very simple contrivance, regulating the pressure at the same time, is that described by F. Krafft (*Berichte*, 15, 1693).

The connection between the boiling points and chemical constitution of compounds will be discussed later in the several homologous groups. Generally the boiling point rises with the complication of the molecule. The unsaturated compounds boil some higher than those saturated. With isomerides having an equally large carbon nucleus those of normal structure possess the highest boiling points. These fall with the accumulation of methyl groups.

It may also be noted that the lower boiling isomerides possess a greater specific volume (*Ber.* 15, 2570).

**Melting Points.** To determine these, introduce the substance into a thin, drawn-out tube, fused shut at one end. This is attached to a thermometer and allowed to dip into a small beaker containing water, or a high boiling compound—paraffin. The beaker is warmed upon a sand bath until the substance in the little tube melts, and the temperature noted. For convenient apparatus for this purpose, see *Berichte*, 10, 1800.

The greater part of the mercury column of the thermometer extends beyond the heated bath, consequently is not as much heated, and, as a result in accurate determinations, a correction must be made. This is done as described with the boiling temperature. Correction for barometric pressure is not required, because the melting points are but slightly affected by pressure.

Very often slight admixtures, which can hardly be excluded, even by fractional crystallization, will materially lower the melting point.

The relation between the melting point and the chemical constitution will be more fully considered under the different homologous groups of bodies.

#### OPTICAL PROPERTIES.

**Refraction.** Like all transparent substances, the carbon compounds possess a variable light refracting power, in which, as known, the quotient of the sine of the angle of refraction ( $r$ ) into the sine of the angle of incidence ( $i$ ) is a constant quantity for every substance. This number is termed the *coefficient of refraction*, or *refractive index* ( $n$ ):

$$\frac{\sin i}{\sin r} = n$$

The coefficient of refraction varies with the temperature, *i. e.*, with the specific gravity of the substance; the expression  $\frac{n-1}{d}$ , in which  $d$  represents the specific gravity, is, however, according to experience, an almost constant quantity for all temperatures, and is called the *specific refractive power*.\*

In a mixture of different liquids, the refractive power  $\left(\frac{N-1}{D}\right)$  is equal to the sum of the refractive powers of the separate constituents  $\left(\frac{n-1}{d}, \frac{n'-1}{d'} \dots\right)$ :

$$\frac{N-1}{D} \cdot 100 = \frac{n-1}{d} \cdot p + \frac{n'-1}{d'} \cdot p' + \frac{n''-1}{d''} \cdot p'' + \dots$$

in which  $p, p', p''$  express the amounts of the ingredients in per

\* The relation between refraction and density is correctly represented, theoretically, by the formula  $\frac{n_2-1}{(n_2+2)d} = \text{a constant}$ ; this leads to the same relations between refraction and chemical constitution, as the simpler expression  $\frac{n-1}{d}$  (see *Berichte* 15, 1031).



cent. From this equation, knowing the coefficients of refraction and the specific gravities of the constituents, the percentage composition of the mixture may be calculated with great accuracy.

An analogous equation answers not only for a mixture of two liquids, but also quite approximately for liquid chemical compounds. In such cases, we designate the product of the specific refractive power and the molecular weight,  $P\left(\frac{n-1}{d}\right)$ , the *molecular refraction*, or the *refractive equivalent*, and the product of the refractive index of the elements, and the atomic weight, the *atomic refraction*; then the proposition finding expression in the preceding equation would read: "The molecular refraction of a liquid carbon compound is equal to the sum of the atomic refractions." The atomic refractions of the elements are deduced from the molecular refractions of the compounds obtained empirically, in the same manner as the atomic volumes are obtained from the molecular volumes (see p 36). These equal, if the refractive index be referred to a ray of infinite wave-length,\* for carbon (in saturated compounds), 4.86; for hydrogen, 1.29; for chlorine, 9.9.

Oxygen has two different "atomic refractions"; if it be united by two affinities to one carbon atom,  $r_A$  equals 3.29, while in its combination with any two atoms  $r_A = 2.71$ . Similarly, sulphur combined with one or two affinities, exhibits different atomic refractions (*Ber.* 15, 2878).

It is worthy of note, that in the unsaturated compounds the doubly combined carbon atoms ( $C = C$ ) possess a greater refractive index, and, indeed, their molecular refraction amounts to about two units more than if calculated from the sum of the above-cited atomic refractions. In accord with this, the derivatives of benzene show a molecular refraction greater, by six units, which would confirm the existence of three double unions in the benzene nucleus. This had already been assumed from chemical considerations. See further, Brühl, *Annalen*, 200, 139, 203, 1 and 255, 211, 121.

These regularities serve, too, for solids, as such, or in solution; the refractive power of a solution equals the sum of the refractive powers of the dissolved substance and the solvent (*Berichte* 16, 3047).

\* The refractive index  $n$  can be determined for any definite wave-length, e. g., for the red ray of the hydrogen light  $H_a$ , which coincides with line C of Fraunhofer, and is then designated  $n_a$ . Since, however, different substances have different dispersive power, such indices are not directly comparable, but require first to be reduced to a ray of infinite wave-length. Indices, freed from the influence of dispersion, are designated with the letter  $A$ . The molecular refraction  $P\left(\frac{A-1}{d}\right)$  of the index  $A$  is designated by  $R_A$ , the atomic refraction by  $r_A$ . For further details, consult Landolt, Poggendorf's *Annalen*, 123, 595.



**Rotation of the Plane of Polarization.\*** Many carbon compounds, liquid and solid, are capable of rotating the plane of polarized light. These are chiefly naturally occurring substances, like the various vegetable acids, amyl alcohol, the sugars, carbohydrates and glucosides, the terpenes and camphors, alkaloids and albuminoids; they are said to be *optically active*. The rotation (of the angle  $\alpha$ ) is proportional to the length  $l$  of the rotating plane, hence, the expression  $\frac{\alpha}{l}$  is a constant quantity. To compare substances of different density, in which very unequal masses fall upon the same plane, these must be referred to like density, and hence, the rotation must be divided by the sp. gr. of the substance at a definite temperature. The expression  $\frac{\alpha}{l \cdot d} = [\alpha]$ , in which the length of the rotating plane is given in decimeters, is called the *specific rotatory power* of a substance at a definite temperature and designated by  $[\alpha]_D$  or  $[\alpha]_j$ , according as the rotation is referred to the yellow sodium line D or the transitional color j. For solid, active substances, with an indifferent solvent, the expression  $[\alpha] = \frac{100 \alpha}{p \cdot l \cdot d}$  will answer; in this  $p$  represents the quantity of substance in 100 parts by weight of the solution, and  $d$  represents the specific gravity of the latter.

The specific rotatory power is constant for every substance at a definite temperature; it varies, however, with the latter, and is also influenced more or less by the nature and quantity of the solvent. Therefore, in the statement of the specific rotatory power of a substance, the temperature and the percentage amount of the solution must be included. By investigating a number of solutions of different concentration, the influence of the solvent may be established and the true specific rotation or the true rotatory constant of the pure substance, designated by  $A_D$ , may then be calculated. The product of the specific rotatory power and the molecular weight  $p$  divided by 100 is designated the molecular rotatory power:—

$$[M] = \frac{P [\alpha]}{100}$$

In crystalline substances, the rotatory power is connected with the crystalline form, and is usually conditioned by the existence of hemihedral planes (*see Tartaric Acids*). As the activity of most of them is retained by solution or is then first perceptible, it is supposed that *crystal molecules* exist in the solution, and that these consist of a union of several chemical molecules. Since, further, numerous solids and liquids are known in dextro- and lævo-rotatory and inactive modifications, in which we can detect no difference in chemical structure, besides the active modifications mostly convertible into inactive, it was concluded that the activity was caused

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\* Compare Landolt, "Optical Rotatory Power," 1879.

not by single chemical molecules, but by groups of *physical molecules*. These were called *physical isomerides*. Since we have ascertained that turpentine oil and camphor, in the form of vapor, possess the same specific rotatory power as when they are in the liquid or solid state, it can no longer be doubted, that the activity can appear as a function of the grouping of the chemical atoms. Of peculiar interest in this connection is the hypothesis of LeBel and van't Hoff, according to which the rotatory power is constantly brought into relation with the chemical structure.\*

According to this theory, the activity of the carbon compounds is influenced by the presence of asymmetric carbon atoms, *i. e.*, by such as are combined with four different atoms or atomic groups—*e. g.*,



The first contains two, the second, however, one asymmetric carbon atom. According to the provisions of Le Bel, such substances with like chemical structure can, in consequence of a different arrangement of the atoms in space, appear in two enantiomorphous forms. These are presumed to cause the optical rotatory power, as well as the varying chemical deportment of the optical modifications. It is, indeed, satisfactorily settled at present, that all active carbon derivatives contain asymmetric carbon atoms. On converting active substances into other derivatives, the activity is retained, providing asymmetric carbon atoms are present; when they disappear the derivatives are inactive. Thus, from the two active tartaric acids are derived the two corresponding active malic acids; whereas, the symmetrical succinic acid, obtained from the latter by further reduction, is inactive. Again, active amyl iodide affords an active ethylamyl and diamyl; on the other hand, an inactive amyl hydride (see Active Amyl Alcohol).

The compounds prepared artificially from inactive substances are almost always inactive; some of them (with asymmetric carbon atoms) can, however, be converted into active modifications. Thus, synthetic inactive tartaric acid, when heated to 170° C., is converted into racemic acid, which is decomposable into levo- and dextro-tartaric acid (see Inactive Tartaric Acid).

Such a splitting up of inactive substances into dextro- and levo-rotatory modifications may be effected by crystallization of the salts (in case of acids their cinchonine salts), as shown with inactive racemic acid, malic acid and mandelic acid. The splitting up and activity can be brought about by ferments. It appears the one active modification is destroyed by the life process of the ferment. Thus, from racemic acid arises levo-rotatory tartaric acid; from inactive amyl alcohol (prepared from active amyl alcohol by boiling with sodic hydrate), the dextro-rotatory alcohol; from synthetic inactive methyl-propyl carbinol and propylene glycol spring the levo-rotatory modifications. Dextro-rotatory mandelic acid is obtained from the synthetic inactive mandelic acid, by the action of *Penicillium glaucum*, while by *Schizomycetes*-fermentation we get the levo-acid (*Berichte*, 15, 1505, 16, 1568 and 2721). All these observations confirm the proposition of Le Bel and van't Hoff, that the asymmetrically constituted inactive carbon derivatives can be broken up into two oppositely active modifications.

\* See van't Hoff, *Die Lagerung der Atome im Raum*, 1877.

## SPECIAL PART.

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The carbon derivatives may be arranged in two classes—the **fatty** and **aromatic** compounds—on the basis of the chemical union of the carbon atoms, and the entire character conditioned by this. The name of the first class is borrowed from the fats and fatty acids comprising it. These were the first derivatives accurately studied. It would be better to name them marsh gas or methane derivatives, inasmuch as they all can be obtained from methane  $\text{CH}_4$ . They are further classified into saturated and unsaturated compounds. In the first of these, called also paraffins, the directly united tetravalent carbon atoms are bound to each other by a single affinity.

The number of  $n$  carbon atoms possessing affinities capable of further saturation, therefore, equals  $2n + 2$  (see p. 26). Their general formula is  $\text{C}_n\text{X}_{2n+2}$ . Here X represents the affinities of the elements or groups directly combined with carbon. The unsaturated compounds result from the saturated by the exit of an even number of affinities in union with carbon. According to the number of affinities yet capable of saturation, the series are distinguished as  $\text{C}_n\text{X}_{2n}$ ,  $\text{C}_n\text{X}_{2n-2}$ , etc. (See p. 26.)

All the aromatic or *benzene* compounds contain a group consisting of six carbon atoms. The simplest derivative of this series is benzene  $\text{C}_6\text{H}_6$  (see p. 27). This accounts for the great similarity in their entire character. Their direct synthesis from the methane derivatives is only possible in exceptional cases; as a usual thing they cannot be converted into the series  $\text{C}_n\text{H}_{2n+2}$ . Their relatively great stability distinguishes them from the fatty bodies. They are generally more reactive, yielding, for instance, nitro-substitution products very readily, and forming various derivatives not possible for the fatty compounds to afford.

The recently investigated trimethylene and tetramethylene derivatives (see p. 28), with which may be included those of furfural, thiophene and pyrrol, may be viewed as the transition stage from the methane compounds containing the open carbon chain, to those of benzene.

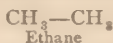
## CLASS I.

## FATTY BODIES, OR METHANE DERIVATIVES.

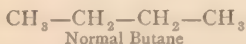
## HYDROCARBONS.

The hydrocarbons show most clearly and simply the different manner in which the carbon atoms are bound to each other. We may regard them as the parent substances from which all other carbon compounds arise by the replacement of the hydrogen atoms by different elements or groups.

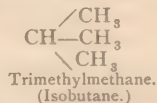
The outlines of the linking of carbon atoms were presented in the Introduction. In consequence of the equivalence (confirmed by facts) of the four affinities of carbon (see p. 24) no isomerides are possible for the first three members of the series  $C_nH_{2n+2}$  :—



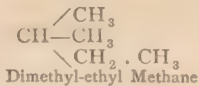
Two structural cases exist for the fourth member  $C_4H_{10}$  :—



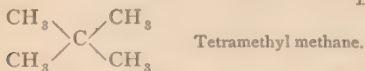
and



For the fifth member, pentane  $C_5H_{12}$ , three isomerides are possible :—

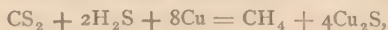


and

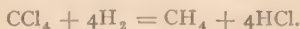


Hexane  $C_6H_{14}$ , the sixth member, has five isomerides (see p. 50). With reference to the different formulation of these hydrocarbons (see p. 47).

*Formation of Hydrocarbons.*—The higher paraffins can be gradually built up synthetically from methane  $\text{CH}_4$ , yet not produced directly from their elements. Methane itself can be synthesized from carbon disulphide  $\text{CS}_2$  (produced by direct union of carbon and sulphur on application of heat) by passing the latter, in form of gas, together with hydrogen sulphide, over red-hot copper—



or by heating with phosphonium iodide; further, by the action of chlorine, carbon disulphide may be changed to carbon tetrachloride, and this reduced, by means of nascent hydrogen (sodium amalgam and water), to methane—



The direct union of carbon and hydrogen has only been observed

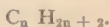


in passing the electric spark between carbon points in a hydrogen atmosphere; the product is acetylene  $C_2H_2$ , which, with additional hydrogen (in presence of platinum black), becomes ethylene  $C_2H_4$ , and then ethane  $C_2H_6$ .

A universal method of producing the hydrocarbons consists in the dry distillation of complex carbon compounds, like wood, lignite and bituminous coal. At higher temperatures, *e. g.*, when their vapors are conducted through red-hot tubes, the hydrocarbons can condense to more complicated bodies, hydrogen separating. Thus, the compounds  $C_2H_6$ ,  $C_2H_4$ ,  $C_6H_6$  (benzene),  $C_{10}H_8$  (naphthalene), and others, are obtained from  $CH_4$ , methane.

A noteworthy formation of the hydrocarbons, especially the paraffins, is that of the action of hydrochloric acid or dilute sulphuric acid, and even steam, upon iron carbide.

### (1) PARAFFINS OR ETHANES.



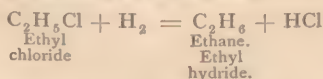
$CH_4$	Methane	$C_6H_{14}$	Hexane
$C_2H_6$	Ethane	$C_7H_{16}$	Heptane
$C_3H_8$	Propane	$C_8H_{18}$	Octane
$C_4H_{10}$	Butane	$C_9H_{20}$	Nonane
$C_5H_{12}$	Pentane	$C_{10}H_{22}$	Decane, etc. (see p. 51).

There is no known limit to these hydrocarbons, or the number of carbon atoms attaching themselves to each other.

Formerly these hydrocarbons were designated as the hydrides of the corresponding radicals or alkyls:  $CH_3$  (methyl),  $C_2H_5$  (ethyl),  $C_3H_7$  (propyl), etc. (see p. 31), because they were first obtained from compounds of these with other elements or groups. Hence the names methyl hydride for methane, ethyl hydride for ethane, etc. The most accessible and first known derivatives of the alkyls  $C_nH_{2n+1}$  were their hydroxides or alcohols, and the halogen ethers of the latter.

The following are the most important methods serving to convert the alkyl  $C_nH_{2n+1}$  derivatives into the corresponding hydrocarbons:—

1. Treat the alkylogens  $C_nH_{2n+1}Cl$  (readily produced from the alcohols  $C_nH_{2n+1}OH$ ) with nascent hydrogen. This may be done by allowing zinc and hydrochloric acid or sodium amalgam to work upon the substance dissolved in alcohol:—

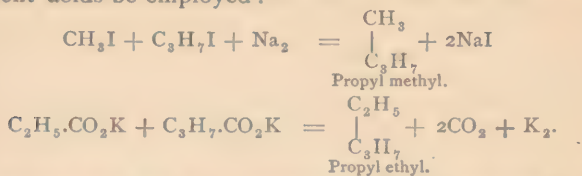


2. Decompose the zinc alkyl compounds with water or the mer-

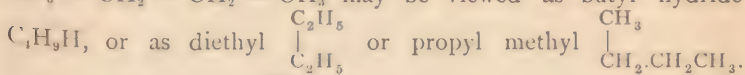




mixture of the iodides of two different alcohol radicals or the salts of different acids be employed :—



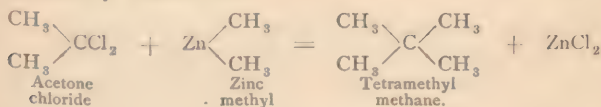
It is known that the hydrocarbons obtained by these different methods are of similar composition and similar structure. Dimethyl is identical with ethyl hydride (ethane); diethyl with methyl propyl or butyl hydride (butane). This follows from a consideration of the structural formulas. Thus, normal butane  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$  may be viewed as butyl hydride



Isobutane  $\text{CH}_3 - \text{CH} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$  can be regarded as isobutyl hydride

$\text{H}\cdot\text{CH}_2 - \text{CH} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$  or as isopropyl methyl  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}(\text{CH}_3)_2 \end{array}$ , or trimethyl methane  $\text{CH}(\text{CH}_3)_3$ , etc. Thus, the various syntheses of a given hydrocarbon may be deduced from its structural formula.

Of other synthetic methods we will yet mention the one employed in the preparation of quaternary hydrocarbons (p. 26). It consists in the action of the zinc alkyls upon so-called acetone chloride and bodies similarly constituted :—



The ethanes arise in the dry distillation of wood, turf, bituminous shales, lignite and bituminous coal, and especially Boghead and cannel coal, rich in hydrogen; hence, they are also present in illuminating gas and the light tar oils. Petroleum contains them already formed. They are, from methane to the highest hydrocarbon, almost the sole constituents of this compound.

The lowest members, up to butane, are gases, at ordinary temperatures, soluble in alcohol and ether. The intermediate members form colorless liquids of faint, characteristic odor, insoluble in water, but miscible with alcohol and ether. The higher members, finally, are crystalline solids (paraffins), soluble in alcohol, more readily in ether. The specific gravities of the liquid and solid

hydrocarbons increase with the molecular weights, but are always less than that of water. The boiling points, too, rise with the molecular weights, and, indeed, the difference for  $\text{CH}_2$  in case of similar structure of homologues, equals  $30^\circ$ , subsequently, with higher members it varies from  $25^\circ$ – $13^\circ$  (see p. 51). The isomerides of normal structure (p. 25) possess the highest boiling points; the lowest are those of the quaternary hydrocarbons. The general rule is—the boiling point of isomeric compounds falls with the accumulation of methyl groups in the molecule.

The paraffins are not capable of saturating any additional affinities; hence, they are not absorbed by bromine or sulphuric acid, being in this way readily distinguished and separated from the unsaturated hydrocarbons. They are slightly reactive and are very stable, hence, their designation as *paraffins* (from *parum affinis*). Fuming sulphuric acid and even chromic acid are without much effect upon them in the cold; when heated, however, they generally burn directly to carbon dioxide and water. When acted upon by chlorine and bromine they afford substitution products:—



Other derivatives may be easily obtained by employing these products.

(1) **Methane**  $\text{CH}_4$  (Methyl hydride) is produced in the decay of organic substances, therefore disengaged in swamps (marsh gas) and mines (coal gas), in which, mixed with air, it forms fire damp.

In certain regions, like Baku in the Caucasus, and the petroleum districts of America, it escapes, in great quantities, from the earth. It is also present, in appreciable amount, in illuminating gas.

The synthesis of methane from  $\text{CS}_2$  and  $\text{CCl}_4$  was noticed upon page 44. It is most conveniently prepared by heating sodium acetate, in a glass retort, with 2 parts of soda-lime:  $\text{CH}_3\text{CO}_2\text{Na} + \text{NaOH} = \text{CH}_4 + \text{CO}_2\text{Na}_2$ .

Methane is a colorless, odorless gas, compressible under great pressure and at a low temperature; its density equals 8 (or 0.5598, air = 1). It is slightly soluble in water, but more readily in alcohol. It burns with a faintly luminous, yellowish flame, and forms an explosive mixture with air:—

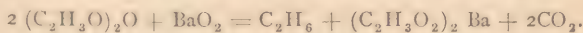


It is decomposed into carbon and hydrogen by the continued passage of the electric spark. When mixed with two volumes of

chlorine it explodes in direct sunlight, carbon separating ( $\text{CH}_4 + 2\text{Cl}_2 = \text{C} + 4\text{HCl}$ ); in diffused sunlight the substitution products  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  are produced.

(2) **Ethane**  $\text{C}_2\text{H}_6$  (Ethyl Hydride, Dimethyl) is a colorless and odorless gas, condensable at  $4^\circ$  and a pressure of 46 atmospheres. Its formation from  $\text{C}_2\text{H}_5\text{I}$ ,  $(\text{C}_2\text{H}_5)_2\text{Zn}$ ,  $\text{CH}_3\text{I}$  and  $\text{CH}_3\cdot\text{CO}_2\text{K}$  corresponds to the given general methods.

To prepare ethane, decompose zinc ethyl with water. It is obtained more conveniently by heating acetic anhydride with barium peroxide:—

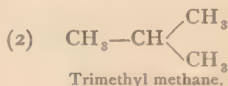


The identity of the ethanes prepared by the various methods is ascertained from their derivatives, and confirmed by their similar heat of combustion (*Berichte*, 14, 501).

Ethane is almost insoluble in water; alcohol dissolves upwards of 1.5 vols. Mixed with an equal volume of chlorine it yields ethyl chloride  $\text{C}_2\text{H}_5\text{Cl}$  in dispersed sunlight; higher substitution products arise with excess of chlorine.

(3) **Propane**  $\text{C}_3\text{H}_8$ , ethyl methyl, occurs dissolved in crude petroleum, and is most conveniently formed by the action of zinc and hydrochloric acid upon the two propyl iodides  $\text{C}_3\text{H}_7\text{I}$ . It is a gas, but becomes a liquid below  $17^\circ$ . Alcohol dissolves upwards of six volumes of it.

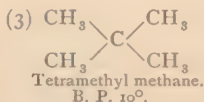
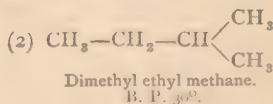
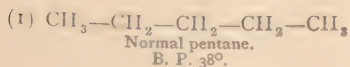
(4) **Butanes**  $\text{C}_4\text{H}_{10}$  (Tetranes). According to the rules of chemical structure, two isomerides correspond to this formula:—



1. *Normal butane* (or diethyl, or propyl methyl, p 47), occurs in crude petroleum, and is obtained synthetically by the action of zinc and sodium upon ethyl iodide  $\text{C}_2\text{H}_5\text{I}$ . It condenses below  $0^\circ$  to a liquid, boiling at  $+1^\circ$ .

2. *Trimethyl methane* or isopropyl methyl, also termed isobutane, is prepared from the iodide of tertiary butyl alcohol  $(\text{CH}_3)_3\text{CI}$  by the action of zinc and hydrochloric acid. It condenses to a liquid at  $-17^\circ$ .

(5) **Pentanes**  $\text{C}_5\text{H}_{12}$ . There are three possible isomerides:—

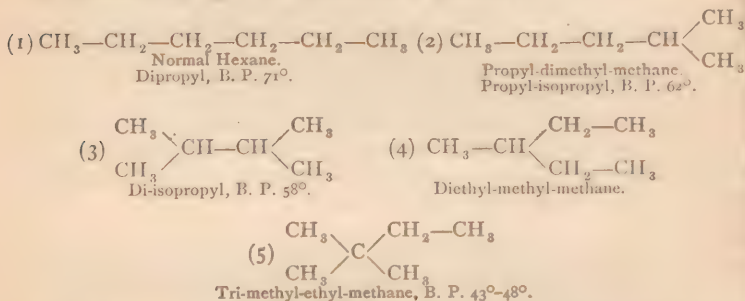


1. *Normal pentane* exists in petroleum and the light tar oils of cannel coal, but has not been obtained by synthesis. It is a liquid, boiling at  $37-39^\circ$ , and having a specific gravity of 0.626 at  $17^\circ$ .

2. *Isopentane* is also present in petroleum, and is obtained from the iodide of the amyl alcohol of fermentation. It is a liquid, boiling at  $30^{\circ}$ ; specific gravity = 0.638 at  $14^{\circ}$ .

3. *Tetramethyl methane* (quaternary pentane) is made by acting upon the iodide  $(\text{CH}_3)_3\text{CI}$  of tertiary butyl alcohol, or upon so called acetone chloride,  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CCl}_2$ , with zinc methyl (comp. p. 47). It is a liquid, boiling at  $9.5^{\circ}$ , and solidifying to a white mass at  $-20^{\circ}$ . The addition of methyl groups constantly lowers the boiling point, but facilitates the transition to the solid state—raises the melting point.

(6) **Hexanes**  $\text{C}_6\text{H}_{14}$ . Five isomerides are possible:—



Four of these are known. *Normal hexane*, occurring in petroleum, may be obtained artificially by the action of sodium upon normal propyl iodide,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ ; by the distillation of suberic acid with barium oxide (p. 46); and further when nascent hydrogen acts on hexyl iodide,  $\text{C}_6\text{H}_{13}\text{I}$  (from mannitol). It boils at  $71.5^{\circ}$ , and has the specific gravity 0.663 at  $17^{\circ}$ .

(7) **Heptanes**  $\text{C}_7\text{H}_{16}$ . Four of the nine possible isomerides are known.

*Normal heptane*,  $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_3$ , is contained in petroleum and the tar oil from cannel coal. Together with octane it constitutes the chief ingredient of commercial ligroïne (p. 52). It is produced in the distillation of azelaic acid  $\text{C}_9\text{H}_{16}\text{O}_4$ , with barium oxide. It boils at  $99^{\circ}$ . Its specific gravity at  $19^{\circ}$  = 0.6967.

(8) **Octanes**  $\text{C}_8\text{H}_{18}$ . Of the eighteen possible isomerides, two are known. Normal octane is present in petroleum and is obtained from normal butyl iodide,  $\text{C}_4\text{H}_9\text{I}$ , by action of sodium (hence Dibutyl), also from sebacylic acid,  $\text{C}_{10}\text{H}_{18}\text{O}_4$ , and from octyl iodide,  $\text{C}_8\text{H}_{17}\text{I}$ . It boils at  $125^{\circ}$ , and its specific gravity at  $0^{\circ}$  = 0.718.

The higher homologues occur in petroleum and tar oils, but cannot be isolated perfectly pure by fractional distillation. The different isomerides are obtained according to the methods already indicated. A series of normal paraffins in pure condition has been prepared by the reduction of the corresponding acids,  $\text{C}_n\text{H}_{2n}\text{O}_2$ , acetones,  $\text{C}_n\text{H}_{2n}\text{O}$ , and alcohols,  $\text{C}_n\text{H}_{2n+2}\text{O}$  (of normal structure). The reduction of acids to paraffins ensues when the former are directly heated to  $200-250^{\circ}$  with concentrated  $\text{HI}$  and amorphous phosphorus; the acetones (ketones) must first be converted into the chlorides,  $\text{C}_n\text{H}_{2n}\text{Cl}_2$ , through the agency of  $\text{PCl}_5$ , and the alcohols also into chlorides,  $\text{C}_n\text{H}_{2n+1}\text{Cl}$ , and alkylens,  $\text{C}_n\text{H}_{2n}$ . In this way the following normal paraffins have been obtained (F. Krafft, *Berichte*, 15, 1687, 1711, 16, 1714):—



		Melting Point.	B. P.	Sp. Gr.*
Nonane .....	$C_9H_{20}$	$-51^\circ$	$149.5^\circ$	0.7330
Decane.....	$C_{10}H_{22}$	$-32^\circ$	$173^\circ$	0.7456
Undecane.....	$C_{11}H_{24}$	$-26.5^\circ$	$194.5^\circ$	0.7745
Dodecane.....	$C_{12}H_{26}$	$-12^\circ$	$214^\circ$	0.773
Tridecane.....	$C_{13}H_{28}$	$-6.2^\circ$	$234^\circ$	0.775
Tetradecane.....	$C_{14}H_{30}$	$+4.5^\circ$	$252.5^\circ$	0.775
Pentadecane .....	$C_{15}H_{32}$	$+10^\circ$	$270.5^\circ$	0.775
Hexadecane .....	$C_{16}H_{34}$	$+18^\circ$	$287.5^\circ$	0.775
Heptadecane.....	$C_{17}H_{36}$	$+22.5^\circ$	$303^\circ$	0.776
Octadecane .....	$C_{18}H_{38}$	$+28^\circ$	$317^\circ$	0.776
Nonadecane.....	$C_{19}H_{40}$	$+32^\circ$	$330^\circ$	0.777
Eicosane.....	$C_{20}H_{42}$	$+36.7^\circ$	$205^\circ$	0.777
Heneicosane .....	$C_{21}H_{44}$	$+40.4^\circ$	$215^\circ$	0.778
Docosane.....	$C_{22}H_{46}$	$+44.4^\circ$	$224.5^\circ$	0.778
Tricosane.....	$C_{23}H_{48}$	$+47.7^\circ$	$234^\circ$	0.778
Tetracosane.....	$C_{24}H_{50}$	$+51.1^\circ$	$243^\circ$	0.778
Heptacosane .....	$C_{27}H_{56}$	$+59.5^\circ$	$270^\circ$	0.779
Hen triacontane.....	$C_{31}H_{64}$	$+68.1^\circ$	$302^\circ$	0.780
Pentatriacontane.....	$C_{35}H_{72}$	$+74.7^\circ$	$331^\circ$	0.781

Under 760 mm. pressure. Under 15 mm. pressure.

The higher normal paraffins, as seen in the table, from hexadecane,  $C_{16}H_{34}$ , forward, are solids at ordinary temperatures, and crystallize readily from alcohol or ether. It is very remarkable that the specific gravities of the higher members are almost equal at their melting points, consequently the molecular volumes are nearly proportional to the molecular weights (*Berichte*, 15, 1719).

The higher members, especially, of this series, are contained in petroleum and the tar oils produced in the distillation of turf, lignite and bituminous coal. To isolate them in a pure condition, crude petroleum or the light tar oils are treated with concentrated sulphuric acid, which dissolves the non-saturated hydrocarbons, *e. g.*,  $C_nH_{2n}$ , and those of the benzene series (in tar oil) and destroys other organic substances. The separated oil is further treated with fuming nitric acid and sodium hydrate, washed with water, dried, and fractionated over metallic sodium. In this way a whole series of hydrocarbons is obtained. From the fraction, boiling from  $0^\circ$  to  $130^\circ$ , of American petroleum two series of hydrocarbons have been isolated, of which those of the first series possess normal structure:—

$C_4H_{10}$	$0^\circ$	—	—
$C_5H_{12}$	$38^\circ$	$C_5H_{12}$	$30^\circ$
$C_6H_{14}$	$71^\circ$	$C_6H_{14}$	$61^\circ$
$C_7H_{16}$	$99^\circ$	$C_7H_{16}$	$91^\circ$
$C_8H_{18}$	$125^\circ$	$C_8H_{18}$	$118^\circ$

The members,  $C_9H_{20}$  to  $C_{16}H_{34}$  (boiling at  $270^\circ$ ), separated from the higher fractions have not been obtained perfectly pure.

Petroleum or rock-oil (naphtha), was probably produced by the

\* The specific gravities correspond to the temperatures at which the bodies melt (for nonane and decane at  $0^\circ$ ).

dry distillation of coal beds, caused by the earth's heat, perhaps, too, by the action of steam upon iron containing combined carbon. It occurs widely distributed in the upper strata of the earth—in Italy, Hungary, Galicia, and in very considerable quantities in the Crimea and the Caucasus (on the shore of the Caspian). Its occurrence in Alsace and Hanover is not very extensive. It is obtained in remarkably large quantities in North America (in Pennsylvania and Canada) by boring. In a crude condition, it is a thick, oily liquid, of brownish color, with greenish lustre. Its more volatile constituents are lost upon exposure to the air; it then thickens and eventually passes into asphaltum. The greatest differences prevail in the various kinds of petroleum; it is only of late years that their thorough study has been commenced.

American petroleum consists almost exclusively of normal paraffins; yet minute quantities of some of the benzene hydrocarbons appear to be present. In a crude form it has a specific gravity of 0.8–0.92, and distils over from 30–360° and beyond this. Various products, valuable technically, have been obtained from it by fractional distillation: *Petroleum ether*, specific gravity 0.665–0.67, distilling about 50–60°, consists of pentane and hexane; petroleum benzine, not to be confounded with the benzene of coal tar, has a specific gravity of 0.68–0.72, distils at 70–90°, and is composed of hexane and heptane; ligroïne, boiling from 90°–120°, consists principally of heptane and octane; refined petroleum, called also kerosene, boils from 150–300° and has a specific gravity of 0.78–0.82. The portions boiling at higher temperatures are applied as lubricants; small amounts of vaseline and paraffins (see below) are obtained from them.

Caucasian petroleum (from Baku) has a higher specific gravity than the American; it contains far less of the light volatile constituents, and distils about 150°. Upwards of 10 per cent. benzene hydrocarbons (isomerides of cumene,  $C_9H_{12}$  and cymene  $C_{10}H_{14}$ ) may be extracted by shaking it with concentrated sulphuric acid. The residue consists almost exclusively of  $C_nH_{2n}$  hydrocarbons, which, according to Beilstein, are hydrogen addition products of the benzene hydrocarbons (like xylene hex-hydride  $C_8H_{16}$ —see this), but, in the opinion of Markownikoff, they are very peculiarly constituted hydrocarbons, that he designates naphthenes (*Berichte* 16, 1873). From its composition, Gallician petroleum occupies a position intermediate between the American and that from Baku (*Annalen*, 220 188).

Products similar to those afforded by American petroleum, are yielded by the tar resulting from the dry distillation of cannel coal (in Scotland) and a variety of coal found in Saxony. The combustible oils obtained from the latter usually bear the names, *photogene* and *solar oil*. Large quantities of solid paraffins are also present in these tar oils.

By *paraffins*, we ordinarily understand the high-boiling (beyond 300°) solid hydrocarbons, arising from the distillation of the tar

obtained from turf, lignite and bituminous shales. They are more abundant in the petroleum from Baku than in that from America. Mineral wax, ozokerite (in Galicia and Roumania) and neftigil (in Baku), are examples existing in a free solid condition. For their purification, the crude paraffins are treated with concentrated sulphuric acid, to destroy the resinous constituents, and then re-distilled. Ozokerite that has been directly bleached, without distillation, bears the name *ceresine*, and is used as a substitute for beeswax. Paraffins that liquefy readily and fuse between  $30-40^{\circ}$ , are known as *vaselines*; they find application as salves.

When pure, the paraffins form a white, translucent, leafy, crystalline mass, soluble in ether and hot alcohol. They melt between  $45^{\circ}$  and  $70^{\circ}$ , and are essentially a mixture of hydrocarbons boiling above  $300^{\circ}$ , but appear to contain also those of the formula,  $C_nH_{2n}$ . Chemically, paraffin is extremely stable, and is not attacked by fuming nitric acid. Substitution products are formed when chlorine acts upon paraffin in a molten state.

The hydrocarbons  $C_{22}H_{46}$ ,  $C_{24}H_{50}$  and  $C_{28}H_{58}$ , were isolated from a commercial paraffin, melting at  $52-54^{\circ}$ , by fractional distillation and crystallization. They have been proved identical with the normal paraffins prepared artificially (see p. 51).

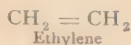
Caucasian ozokerite consists mainly of one hydrocarbon (called lekene) melting at  $79^{\circ}$ , and having the composition,  $C_nH_{2n+2}$  or  $C_nH_{2n}$  (*Berichte*, 16, 1548).

## (2) UNSATURATED HYDROCARBONS $C_nH_{2n}$ .

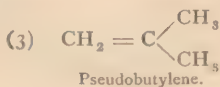
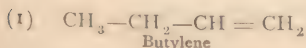
### ALKYLENS OR OLEFINES.

$C_2H_4$	Ethylene	$C_6H_{12}$	Hexylene
$C_3H_6$	Propylene	$C_7H_{14}$	Heptylene
$C_4H_8$	Butylene	$C_8H_{16}$	Cetene
$C_5H_{10}$	Amylene	$C_{30}H_{60}$	Melene.

The hydrocarbons of this series contain two hydrogen atoms less than the first series. In their general structure, two adjacent carbon atoms are united by two affinity units each—by double binding (see p. 28):



Three structural cases are possible for the third member—



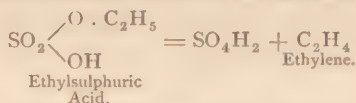
Five isomerides of the formula  $C_5H_{10}$  are possible.\* The most important general methods for the preparation of these hydrocarbons are:—

(1) Distil the monohydric alcohols  $C_nH_{2n+1}OH$  with dehydrating agents, *e. g.* sulphuric acid, chloride of zinc, and phosphorus or boron trioxide. These remove one molecule of water.



The secondary and tertiary alcohols decompose with special readiness. The higher alcohols not volatile without decomposition, suffer the above change when heat is applied to them; thus cetene,  $C_{16}H_{32}$ , is formed on distilling cetyl alcohol,  $C_{16}H_{34}O$ .

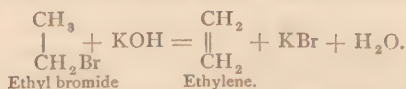
When sulphuric acid acts upon the alcohols, acid esters of sulphuric acid (the so-called acid ethereal salts—see these) appear as intermediate products. When heated these break up into sulphuric acid and  $C_nH_{2n}$  hydrocarbons—



The higher olefines may be obtained from the corresponding alcohols by distilling the esters they form with the fatty acids. The products are an olefine and an acid (*Berichte* 16, 3018):—

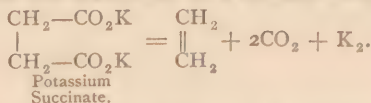


(2) The halogen derivatives, readily formed from the alcohols, are digested with alcoholic sodium or potassium hydrate—



In this reaction also, the haloid (especially the iodides) derivatives corresponding to the secondary and tertiary alcohols break up very readily. Heating with lead oxide effects the same result (*Berichte* 11, 414).

(3) Electrolyse the alkali salt of a dibasic acid (see p. 46)—

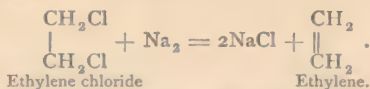


This reaction is perfectly analogous to the formation of the dialkyls from the monobasic fatty acids (see p. 47).

\* The ring-shaped atomic linkings, exemplified in trimethylene  $C_3H_6$  and tetramethylene  $C_4H_8$  (see p. 28) are not included here. Their properties are different from those of the alkylens, and they at the same time form a transition to the closed ring of benzene. For this reason they will be considered after the fatty bodies.

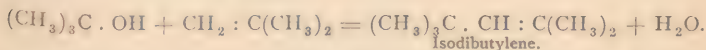


(4) The olefines also result, on heating some of the dihalogen compounds  $C_nH_{2n}X_2$  with sodium—



Synthetically the olefines can be prepared according to methods similar to those employed with normal hydrocarbons (see p. 44).

Worthy of note is the formation of higher alkylens in the action of lower members with tertiary alcohols or alkyl-iodides. Thus from tertiary butyl alcohol and isobutylene, with the assistance of zinc chloride or sulphuric acid, we get isodibutylene (*Annalen* 189, 65):



In an analogous way we obtain tetramethyl ethylene (*Berichte* 16, 398) on heating  $\beta$ -isoamylene (see p. 59) with methyl iodide and lead oxide.

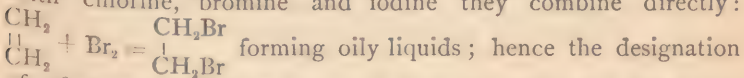


In the dry distillation of many complicated carbon compounds, the olefines are produced along with the normal paraffins, hence their presence in illuminating gas and in tar oils.

As far as physical properties are concerned the olefines resemble the normal hydrocarbons; the lower members are gases, the intermediate ethereal liquids, while the higher (from  $C_{16}H_{32}$  up) are solids. Generally their boiling points are a few degrees higher than those of the corresponding paraffins.

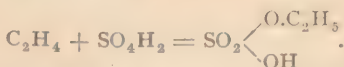
Being unsaturated, they can unite directly with two univalent atoms or groups; then the double binding becomes single.

With chlorine, bromine and iodine they combine directly:



of ethylene as olefant gas, and that of *olefines* for the entire series. The liquid olefines react very energetically with bromine; on this account they should be cooled and diluted with ether.

Concentrated sulphuric acid absorbs them, forming ethereal salts:—



Very often the absorption takes place only at high temperatures.

They combine, too, directly with HCl, HBr and especially readily with HI.



They yield so-called chlorhydrins with aqueous hypochlorous acid:—



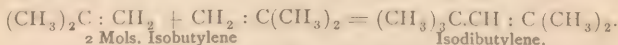
Nascent hydrogen (zinc and hydrochloric acid, or sodium amalgam) converts the olefines into the saturated hydrocarbons:  $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$ .

Concentrated hydriodic acid effects the same if aided by heat, and, especially, when phosphorus is present. The iodide formed at first is reduced by a second molecule of HI:—



*Polymerisation of Olefines.* When acted upon by dilute hydrochloric acid, zinc chloride, boron fluoride and other substances, many olefines sustain, even at ordinary temperatures, a polymerisation, in consequence of the union of several molecules. Thus there result from isoamylenes  $\text{C}_5\text{H}_{10}$ : di-isoamylenes  $\text{C}_{10}\text{H}_{20}$ ; tri-isoamylenes  $\text{C}_{15}\text{H}_{30}$ , etc., etc. Butylene and propylene behave in the same way. Ethylene, on the other hand, is neither condensed by sulphuric acid nor boron fluoride. The polymerides act like unsaturated compounds, and are capable of binding two affinities.

The nature of the binding of the carbon atoms in polymerisation is, in all probability, influenced by the different structure of the alkylens. The manner of formation and structure of the isodibutylene produced from isobutylene correspond to the formulas —



Tertiary butyl alcohol very probably figures as an intermediate product, and afterwards unites with a second molecule of isobutylene, and condenses to isodibutylene (compare p. 55).

Although ethylene suffers no alteration, yet its substitution products polymerize very readily.

Potassium permanganate and chromic acid oxidize the olefines, causing the molecules to break their double union (*Annalen* 197, 225), while the two components are further oxidized to acids and ketones. Thus butylene  $\text{CH}_3\text{CH}_2\text{CH} : \text{CH}_2$  is obtained from propionic and formic acids; but from tetra-methyl-ethylene  $(\text{CH}_3)_2\text{C} : \text{C}(\text{CH}_3)_2$  we get 2 molecules of acetone  $(\text{CH}_3)_2\text{CO}$ .

**Methylene**  $\text{CH}_2$ , the first member of the series  $\text{C}_n\text{H}_{2n}$ , does not exist. In all the reactions in which it might be expected to occur, for instance, when copper acts on methylene iodide  $\text{CH}_2\text{I}_2$ , we obtain only polymerides: ethylene  $\text{C}_2\text{H}_4$ , propylene  $\text{C}_3\text{H}_6$ , etc.

(1) **Ethylene**  $C_2H_4$  (olefiant gas) forms in the dry distillation of many organic substances, and hence is present in illuminating gas (6 per cent.). It is best prepared by the action of sulphuric acid upon ethyl alcohol.

A mixture of 1 vol. 80 per cent. alcohol and 6 vols. sulphuric acid is permitted to stand for awhile, then heated, in a capacious vessel, upon a sand bath. The foaming may be prevented by the addition of sand. The liberated gas is conducted through a vessel containing potassium hydrate, to remove  $CO_2$  and  $SO_2$ , and, finally, collected over water (*Annalen*, 192, 244).

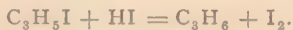
Ethylene is a colorless gas, with a peculiar, sweetish odor. Its sp. gr. equals 14 ( $H = 1$ ). Water dissolves but slight quantities of it, while alcohol and ether absorb about 2 volumes. It is liquefied at  $0^\circ$ , and a pressure of 45 atmospheres. At ordinary pressure it boils at  $-105^\circ$ , and is suitable for the production of very low temperatures. It burns with a bright, luminous flame, decomposing into  $CH_4$  and C. In chlorine gas the flame is very smoky; a mixture of ethylene and chlorine burns away slowly when ignited. It forms a very explosive mixture with oxygen (3 volumes).

When in alcoholic solution ethylene combines readily with chlorine, bromine and iodine. Fuming hydriodic acid absorbs it with formation of  $C_2H_5I$ . Aided by platinum black it will combine with  $H_2$  at ordinary temperatures, yielding  $C_2H_6$ . At the ordinary temperature it combines with sulphuric acid only after continued shaking; the absorption is, however, rapid and complete at  $160-174^\circ$ . By boiling the resulting ethylsulphuric acid with water we can get alcohol. Potassium permanganate oxidizes ethylene to oxalic and formic acids; with chromic acid ethylene yields aldehyde.

(2) **Propylene**  $C_3H_6 = CH_3.CH:CH_2$  is obtained from many organic substances, *e. g.*, amyl alcohol, when their vapors are conducted through red-hot tubes. Propyl and isopropyl iodide are converted into it when boiled with alcoholic potash—



The same end is achieved by the action of nascent hydrogen (zinc and hydrochloric acid) or hydriodic acid upon allyl iodide:



*Preparation.*—1. Digest a mixture of 80 gr. isopropyl iodide, 50 gr., 95 per cent. alcohol, and 50 gr. KOH upon a water bath; at  $40-50^\circ$  already a regular stream of propylene escapes. 2. A solution of allyl iodide in glacial acetic acid, or, better, one in alcohol, is allowed to drop upon granulated zinc.

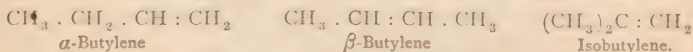
Propylene is a gas, liquefiable under great pressure. It combines directly with the halogens and their hydrides. Concentrated  $H_2SO_4$  dissolves it with formation of isopropyl sulphuric acid and

polymeric propylenes  $(C_3H_6)_n$ . It dissolves in concentrated HI, yielding isopropyl iodide—



Trimethylene  $C_3H_6$ , isomeric with propylene, is obtained from trimethylene bromide (see p. 74), by aid of sodium. Unlike propylene, it unites with difficulty with bromine and HI, to trimethylene bromide (to normal propyl iodide). It appears to contain a closed carbon chain (see p. 28), and, with its derivatives, is considered after the fatty bodies.

(3) **Butylenes**  $C_4H_8$ .—Theoretically, three isomerides are possible—



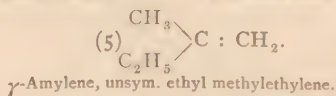
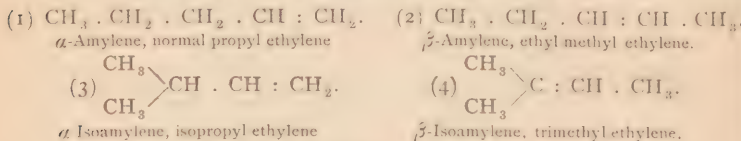
(1) *a*-Butylene (normal Butylene) is formed from normal butyl iodide  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$ , by aid of alcoholic potash; and also from brom-ethylene and zinc-ethyl:  $2CH_2 : CHBr + (C_2H_5)_2Zn = 2CH_2 : CH \cdot C_2H_5 + ZnBr_2$ . In the cold it condenses to a liquid, boiling at  $-5^\circ$ . With HI, it forms secondary butyl iodide,  $CH_3 \cdot CH_2 \cdot CHI \cdot CH_3$ . Its bromide,  $C_4H_8Br_2$ , boils at  $66^\circ$ .

(2) *β*-Butylene (pseudo-butylene) results from secondary butyl iodide (see above) and alcoholic potash or mercuric cyanide; also (together with isobutylene) from isobutyl alcohol, in which case there occurs a molecular transposition. It boils at  $+1^\circ$  and solidifies on cooling. It yields secondary butyl iodide with HI. Its bromide,  $C_4H_8Br_2$ , boils at  $159^\circ$ , and is changed by alcoholic potash to crotonylene  $CH_3 \cdot C : C \cdot CH_3$  (p. 63).

(3) *Isobutylene* is obtained from isobutyl iodide  $(CH_3)_2CHI \cdot CH_2I$  and tertiary butyl iodide  $(CH_3)_3CI$ , when alcoholic potash acts upon them; further, from isobutyl alcohol  $(CH_3)_2 \cdot CH \cdot CH_2OH$ , when heated with zinc chloride or sulphuric acid. Pseudo-butylene appears at the same time (*Berichte*, 13, 2395 and 2404, 16, 2284). It boils at  $-6^\circ$  and dissolves in sulphuric acid (diluted one-half with water) forming butyl-sulphuric acid. The latter affords trimethyl carbinol, when boiled with water. Concentrated HI absorbs isobutylene with formation of tertiary butyl iodide. Its bromide boils at  $149^\circ$ .

When isobutylene is digested with  $H_2SO_4$  and  $H_2O$  (equal volumes) it becomes isodibutylene  $(CH_3)_3C \cdot CHI : C(CH_3)_2$ , boiling at  $130^\circ$  (see p. 56).

(4) **Amylenes**  $C_5H_{10}$ .—Five isomerides are theoretically possible:—



(1) *a*-Amylene  $C_5H_{10} \cdot CH : CH_2$  (normal amylenes, propylethylene) has not yet been prepared in a pure condition; it appears to be that part of ordinary amylenes (see below) which is insoluble in sulphuric acid, boils about  $37^\circ$  and is oxidized by a  $KMnO_4$  solution to butyric and formic acids (*Annalen*, 197, 253). It unites with HI to the iodide  $C_5H_{10} \cdot CHI \cdot CH_3$ , boiling at  $144^\circ$ .

(2)  $\beta$ -Amylene  $C_2H_5 \cdot CH : CH \cdot CH_3$  (sym. ethylmethyl-ethylene) is produced from the iodide  $C_2H_5 \cdot CHI \cdot C_2H_5$  of diethylcarbinol, boiling at  $145^\circ$ . The boiling point of  $\beta$ -amylenes is  $36^\circ$ ; with HI it yields the same iodide as  $\alpha$ -amylenes. Its bromide,  $C_3H_7Br$ , boils at  $178^\circ$ .

(3)  $\alpha$ -Isoamylenes,  $(CH_3)_2CH \cdot CH : CH_2$ , (isopropyl ethylene) is formed together with  $\gamma$ -amylenes, from the iodide of the amyl alcohol of fermentation (see this), by the action of alcoholic potash (*Annalen*, 190, 351). A mixture of these two amylenes results, and boils at  $23-27^\circ$ . On shaking with cold  $H_2SO_4$  (diluted one-half with water) the  $\gamma$ -variety dissolves, leaving  $\alpha$ -isoamylenes unaltered (about 60 per cent. of the mixture). Similarly, by action of HI (or HBr) upon the mixture at  $-20^\circ$ ,  $\gamma$  amylenes are changed to the iodide, while  $\alpha$ -amylenes are not affected. Isoamylenes boil at  $21.1^\circ-21.3^\circ$ . It does not unite in the cold (below  $0^\circ$ ) with  $H_2SO_4$ , HI, or HBr. At ordinary temperatures it combines gradually with HI, HBr, and HCl, yielding derivatives of methyl isopropyl carbinol  $(CH_3)_2 \cdot CH \cdot CHX \cdot CH_3$ .

(4)  $\beta$ -Isoamylenes  $(CH_3)_2 \cdot C : CH \cdot CH_3$  (trimethyl ethylene), produced from the iodides of methyl isopropyl carbinol  $(CH_3)_2 \cdot CHI \cdot CHI \cdot CH_3$ , and dimethyl-ethyl carbinol  $(CH_3)_2 \cdot CI \cdot CH_2 \cdot CH_3$ , boils at  $36-38^\circ$ . At ordinary temperatures it reunites with HI to the iodide  $(CH_3)_2 \cdot CI \cdot CH_2 \cdot CH_3$ . It combines readily, in the cold, with sulphuric acid to the sulphuric ether, and the latter, when boiled with water, affords dimethyl-ethyl carbinol  $(CH_3)_2 \cdot C(OH) \cdot CH_2 \cdot CH_3$ .

$\beta$ -Isoamylenes are the chief ingredient of the ordinary amylenes obtained from fermentation amyl alcohol by distillation with zinc chloride. (See *Annalen*, 190, 332.) The product, boiling about  $25-40^\circ$ , is a mixture of  $\beta$ -isoamylenes (50 per cent.) with pentane (boiling about  $29^\circ$ ) and probably contains, in addition,  $\gamma$ -amylenes and also  $\alpha$ -amylenes. On shaking crude amylenes in the cold ( $-20^\circ$ ) with sulphuric acid, diluted with  $\frac{1}{2}$ -1 vol. of  $H_2O$ , the  $\beta$ -isoamylenes dissolve (also any  $\gamma$ -amylenes that may be present) to amyl-sulphate, which affords dimethyl-ethyl carbinol,  $(CH_3)_2 \cdot C(OH) \cdot CH_2 \cdot CH_3$ . The chief constituents of the undissolved oil are pentane and  $\alpha$ -amylenes, which are oxidized by  $KMnO_4$  to butyric and formic acids (p. 58). On shaking ordinary crude amylenes with  $H_2SO_4$  (diluted with  $\frac{1}{2}$  vol. water), without cooling, polymeric amylenes are produced: diamylenes,  $C_{10}H_{20}$ , boiling at  $156^\circ$ , triamylenes,  $C_{15}H_{30}$ , boiling at  $240-250^\circ$ , and tetramylenes, boiling about  $360^\circ$ . All these are oily liquids, which combine with bromine.

(5)  $\gamma$ -Amylenes,  $\begin{array}{c} CH_3 \\ \diagdown \\ C_2H_5 \end{array} C : CH_2$ , (unsym. methyl-ethyl ethylene) is contained (40 per cent.) in crude amylenes, obtained from the iodide of fermentation amyl alcohol (see above 3), hence, very probably also present in ordinary amylenes. It very likely comes from the active alcohol,  $\begin{array}{c} CH_3 \\ \diagdown \\ C_2H_5 \end{array} CH \cdot CH_2 \cdot OH$ , present in the fermentation alcohol, although itself not active. It cannot be isolated because of its very ready union with  $H_2SO_4$  and HI, even in the cold. Both the sulphuric acid ether from it and the iodide yield tertiary amyl alcohol. The iodide of active amyl



alcohol furnishes an amylene boiling at  $31^{\circ}$  (Le Bel). This is probably pure  $\gamma$ -amylene. It gives the chloride,  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{matrix} \text{CCl} \cdot \text{CH}_3$ , with  $\text{HCl}$ . This boils at  $87^{\circ}$ , and decomposes with alcoholic potash into  $\beta$ -isoamylene.

Various higher olefines have been prepared from the corresponding alcohols. The highest can be made by the distillation of the esters derived from the alcohols and the higher fatty acids (p. 54). In this way the following olefines of normal structure have been prepared:

		Melting Point.	B. P. at 15 mm.	Sp. Gr.
Dodecylene.....	$\text{C}_{12}\text{H}_{24}$	$-31.5^{\circ}$	$96^{\circ}$	0.7954
Tetradecylene.....	$\text{C}_{14}\text{H}_{28}$	$-12^{\circ}$	$127^{\circ}$	0.7936
Hexadecylene.....	$\text{C}_{16}\text{H}_{32}$	$+4^{\circ}$	$154^{\circ}$	0.7917
Octoddecylene.....	$\text{C}_{18}\text{H}_{36}$	$+18^{\circ}$	$179^{\circ}$	0.7910

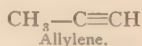
Hexadecylene,  $\text{C}_{16}\text{H}_{32}$ , is sometimes called *cetene*; it was first obtained from cetyl alcohol, and at ordinary temperatures boils about  $274^{\circ}$ . Cerotene, from Chinese wax, melts at  $58^{\circ}$ , while melene,  $\text{C}_{30}\text{H}_{60}$ , from ordinary wax, melts at  $62^{\circ}$ .

### (3) HYDROCARBONS $\text{C}_n\text{H}_{2n-2}$ .

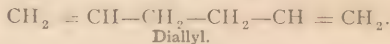
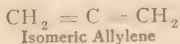
#### ACETYLENE SERIES.

$\text{C}_2\text{H}_2$ Acetylene	$\text{C}_5\text{H}_8$ Valerylene
$\text{C}_3\text{H}_4$ Allylene	$\text{C}_6\text{H}_{10}$ Hexoylene.
$\text{C}_4\text{H}_6$ Crotonylene	

The above hydrocarbons, differing from the normal  $\text{C}_n\text{H}_{2n+2}$  by four atoms of hydrogen, may be based upon two structurally different but possible formulas. In one case we assume a triple union of two neighboring carbon atoms—



while in the second a double union occurs twice—

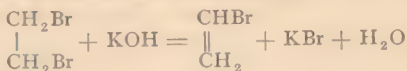


This structural difference is abundantly manifest in the varying chemical behavior, since only members of the first class (having the group  $\equiv\text{CH}$ ) that can be regarded as true acetylenes, possess the power of entering into combination with copper and silver, affording derivatives in which the H of the group  $\equiv\text{CH}$  is replaced by metals (see p. 61).

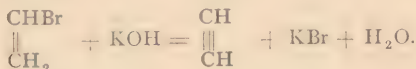
The hydrocarbons of this series are produced according to the same methods as those of the ethylene series. They are formed on heating the haloids  $\text{C}_n\text{H}_{2n-1}\text{X}$  (corresponding to the alcohols of



the allyl series) and  $C_nH_{2n}X_2$  with alcoholic potash; in the latter case the reaction proceeds in two phases—

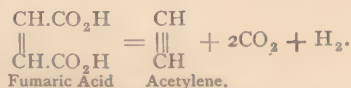


and



Regarding the regularity of exit of the halogen-hydride in higher homologues compare *Berichte* 10, 2058.

They also arise in the electrolysis of unsaturated dibasic acids (compare p. 54).



As unsaturated compounds of second degree, the hydrocarbons  $C_nH_{2n-2}$  are capable of adding to themselves four affinity units. Hence they unite with one and two molecules of the halogens and their hydrides. Thus acetylene forms  $C_2H_2Br_2$  and  $C_2H_2Br_4$ . They are absorbed by concentrated sulphuric acid with formation of sulphuric ethers and condensation occurs at the same time. Nascent hydrogen converts them into the hydrocarbons  $C_nH_{2n}$  and  $C_nH_{2n+2}$ .

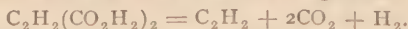
In the presence of  $HgBr_2$  and other salts of mercury, the acetylenes can unite with water. In this way we get from acetylene, aldehyde  $C_2H_4O$ , from allylene  $C_3H_4$ , acetone  $C_3H_6O$ , from valerylene  $C_5H_8$ , a ketone  $C_5H_{10}O$  (*Berichte* 14, 1542 and 17, 28). Very often moderately dilute sulphuric acid will act in the same way (see Allylene).

A characteristic of the true acetylenes is their power to yield solid crystalline compounds by the action of ammoniacal solutions of silver and copper salts. Hydrochloric acid will again liberate the acetylenes from these salts. A very convenient method for separating the acetylenes from other gases and for preparing them pure, is based on this fact.

Like the alkylens (p. 56) the acetylenes condense, and in this manner we very frequently obtain bodies that belong to the benzene series. At a red heat benzene  $C_6H_6$  is obtained from acetylene  $C_2H_2$ ; mesitylene  $C_9H_{12}$  (trimethylbenzene  $C_6H_3(CH_3)_3$ ) from allylene  $C_3H_4$  by the action of sulphuric acid, and hexamethyl benzene  $C_{12}H_{18}$  (see p. 63) from crotonylene  $C_4H_6$ .

**Acetylene**  $C_2H_2$  is formed when many carbon compounds, like alcohol, ether, marsh gas, methylene, etc., are exposed to intense heat (their vapors conducted through tubes heated to redness).

Hence it is present in illuminating gas, to which it imparts a peculiar odor. Its direct synthesis from carbon and hydrogen is described on p. 45; acetylene results, too, in the decomposition of calcium carbide by water. Its formation in the electrolysis of the alkali salts of fumaric and maleic acids is significant:



It is produced when silver, copper or zinc dust acts upon iodoform.

*Preparation.*—1. Ethylene bromide  $\text{C}_2\text{H}_4\text{Br}_2$  is heated with two parts of KOH and strong alcohol, in a flask provided with an upright condenser. The escaping gas is conducted through an ammoniacal silver solution, the precipitate washed with water and decomposed by hydrochloric acid (*Annalen* 191, 368). 2. Let the flame of a Bunsen burner strike back, *i. e.*, burn within the tube, and then aspirate the gases through a silver solution (Berthelot's apparatus).

Acetylene is a gas of peculiar, penetrating odor, and may be liquefied at  $+1^\circ$  and under a pressure of 48 atmospheres. It is slightly soluble in water; more readily in alcohol and ether. It burns with a very smoky flame. The color of the copper compound  $\text{C}_2\text{HCu} \cdot \text{CuOH}$  is red, while that of the silver  $\text{C}_2\text{HAg} \cdot \text{AgOH}$  is white; their composition is not definitely established. When heated, both explode very violently. When acetylene is conducted through ammoniacal silver chloride, a white, curdy precipitate  $\text{C}_2\text{HAg} \cdot \text{AgCl}$  is thrown out of solution. Sodium heated in acetylene gas disengages hydrogen, and we obtain the compounds  $\text{C}_2\text{HNa}$  and  $\text{C}_2\text{Na}_2$ .

Nascent hydrogen (zinc and ammonia) converts acetylene into  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ ; and when hydrogen and acetylene are passed over platinum black  $\text{C}_2\text{H}_6$  is formed.

Acetylene reacts very energetically with chlorine gas. It forms a crystalline compound with  $\text{SbCl}_5$ , but heat changes this to dichlor-ethylene  $\text{CHCl} : \text{CHCl}$  and  $\text{SbCl}_3$ . With bromine it forms  $\text{C}_2\text{H}_2\text{Br}_2$  and  $\text{C}_2\text{H}_2\text{Br}_4$ . If the first of these is digested with alcoholic potash, it is altered to monobrom-acetylene  $\text{C}_2\text{HBr}$ , a gas, inflaming in contact with air. An explosive gas, monochlor-acetylene  $\text{C}_2\text{HCl}$ , is obtained from dichloracrylic acid.

**Allylene**,  $\text{C}_3\text{H}_4 = \text{CH}_3 - \text{C} \equiv \text{CH}$ . We get this by the action of alcoholic potash upon monochlor-propylene  $\text{CH}_3 \cdot \text{CCl} : \text{CH}_2$ , and by heating dichloracetone chloride  $\text{CH}_3 \cdot \text{CCl}_2 \cdot \text{CHCl}_2$  with sodium; further, in the electrolysis of the alkali salts of mesaconic and citraconic acids. It is very similar to acetylene. Its copper compound is siskin green in color; the silver derivative  $\text{C}_3\text{H}_3\text{Ag}$  is white. Allylene forms the compound  $(\text{C}_3\text{H}_3)_2\text{Hg}$  with mercuric oxide. This crystallizes from alcohol in brilliant needles; acids decompose it into allylene and a mercury salt. With bromine we get the liquid bromides  $\text{C}_3\text{H}_4\text{Br}_2$  and  $\text{C}_3\text{H}_4\text{Br}_4$ ; and with two molecules of the halogen hydrides the compounds  $\text{CH}_3 \cdot \text{CX}_2 \cdot \text{CH}_3$ .

Allylene is soluble in concentrated sulphuric acid; a large quantity of acetone is produced by diluting this solution with

water; but on distilling it the allylene condenses to mesitylene:  $3C_3H_4 = C_9H_{12}$  a benzene derivative. In the presence of mercury salts, allylene combines with water to form acetone (see p. 61).

**Isomeric Allylene**,  $CH_2:C:CH_2$ . This does not unite with copper and silver. It is produced by the electrolysis of potassium itaconate; by the action of sodium upon dichlor-propylene  $C_3H_4Cl_2$  (from dichlorhydrin, see glycerol) and probably too from allyl iodide. With bromine it forms a tetrabromide  $C_3H_4Br_4$  crystallizing in leaflets and melting at  $195^\circ$ .

Crotonylene,  $C_4H_6$ , Valerylene  $C_5H_8$ , Hexoylene  $C_6H_{10}$ , or Butine, Pentine, Hexine, etc., are the higher members of the series  $C_nH_{2n-2}$ .

**Crotonylene**,  $CH_3C:CCH_3$ —dimethyl acetylene, is a strong smelling liquid obtained from the bromide of pseudo-butylene  $CH_3CH:CHCH_3$ , by the action of alcoholic potash. Its boiling point is  $18^\circ$ . When it is shaken with sulphuric acid (diluted  $\frac{1}{3}$  with water), it is converted into solid hexamethyl benzene  $C_6(CH_3)_6$ , melting at  $164^\circ$ :—



**Diallyl**,  $CH_2:CH.CH_2.CH_2.CH:CH_2$ , is produced when sodium or silver acts upon allyl iodide (see p. 71), and by distilling allyl mercury iodide  $C_3H_5HgI$ , with potassium cyanide. It boils at  $59^\circ$  and forms a crystalline tetrabromide  $C_6H_{10}Br_4$ , melting at  $63^\circ$ . As it does not contain the group  $\equiv CH$ , it forms no metal derivatives.

#### (4) HYDROCARBONS $C_nH_{2n-4}$ .

Various bodies of this series have been obtained from the tar oil (from cannell coal) boiling as high as  $300^\circ$ . In all probability they result from the polymerization of the hydrocarbons  $C_nH_{2n-2}$ , contained in the coal tar, through the agency of sulphuric acid.

The lowest member of this series would be vinyl acetylene  $C_4H_4 = CH_2:CH.C:CH$ . It has not been isolated. Its homologue is

**Valylene**,  $C_5H_6$ , with the structure  $CH_3CH:CH.C:CH$  or  $CH_2:C(CH_3).C:CH$ . This is obtained from valerylene dibromide  $C_5H_8Br_2$ , by the action of alcoholic potassium hydroxide. It boils at  $50^\circ$ , and has an alliaceous odor. It forms precipitates with ammoniacal copper and silver solutions, and yields the hexabromide  $C_5H_6Br_6$ , with 6 atoms of bromine.

The terpenes  $C_{10}H_{16}$ , which are hydrogen addition products of benzene compounds, are homologues of these hydrocarbons.

#### (5) HYDROCARBONS $C_nH_{2n-6}$ .

The only hydrocarbon of the fatty series belonging here is—

**Dipropargyl**,  $C_6H_6 = CH:C.CH_2.CH_2.C:CH$ . This is isomeric with benzene, but its properties are entirely different. On warming solid crystalline diallyl-tetrabromide  $C_6H_{10}Br_4$  (see above) with KOH, there is formed dibrom-diallyl  $C_6H_8Br_2$  (together with a little dipropargyl), a liquid boiling at  $205-210^\circ$ . On treating the latter compound with alcoholic potash we obtain dipropargyl  $C_6H_6$ . This is a very mobile liquid, of penetrating odor, and boiling at  $85^\circ$ ; its specific gravity at  $18^\circ$  equals 0.81.

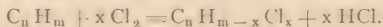
The compound  $C_6H_4Cu_2 \cdot 2H_2O$ , which it forms with ammoniacal copper solutions is siskin yellow in color; that with silver  $C_6H_4Ag_2 \cdot 2H_2O$  is white, but blackens on exposure to the air. Acids again liberate dipropargyl from these.

If dipropargyl be allowed to stand, or if heat be applied to it, it polymerizes and becomes thick and resinous. It unites energetically with bromine to  $C_6H_6Br_4$  and  $C_6H_6Br_8$ ; the latter melts at  $140^\circ$ .

## HALOGEN DERIVATIVES OF THE HYDROCARBONS.

The so-called halogen substitution products result from the replacement of hydrogen in the hydrocarbons by the halogens. In general character they resemble the compounds from which they have their origin. The following are the most important methods for their preparation—

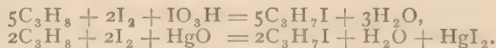
(1) By direct action of the halogens upon the hydrocarbons, when one or all the hydrogen atoms will suffer replacement, the hydrides of the halogens forming at the same time :—



The action of chlorine is accelerated, and very often also dependent upon direct sunlight or the presence of small quantities of iodine. It is the  $ICl_3$ , which arises in the latter case, that facilitates the reaction.  $SbCl_5$  also plays the role of a chlorine carrier, since upon heating it yields  $SbCl_3$  and  $2Cl$ . The same may be remarked of  $MoCl_5$ . When the chlorination is very energetic a rupture of the carbon linking takes place (*Berichte*, 8, 1296. 10, 801). Heat hastens the action of bromine. Usually iodine does not replace well, inasmuch as the final iodine products sustain reduction through the hydriodic acid formed simultaneously with them :—

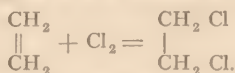


In the presence of substances (like  $HIO_3$  and  $HgO$ ) capable of uniting or decomposing  $HI$ , iodine frequently effects substitution :—



In direct substitution a mixture of mono- and poly-substitution products generally results, and these are separated by fractional distillation or crystallization.

(2) By adding halogens to the unsaturated hydrocarbons :—



At ordinary temperatures, chlorine and bromine react very violently ; in the absence of light the action is more regular, and when it is present, substitution products also arise. Iodine (in alcoholic solution) generally enters combination only upon application of heat.

(3) By adding halogen hydrides to the unsaturated hydrocarbons. In concentrated aqueous solution,  $HI$  reacts very readily :—

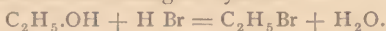


Here again we observe the common rule that the halogen atom almost invariably attaches itself to the least hydrogenized carbon atom (*Annalen*, 179, 296 and 325).

(4) By replacing the hydroxyl groups of the alcohols  $C_n H_{2n+1} OH$  by halogens. This is the most convenient method of preparing the mono-halogen products, as the alcohols are very readily obtained.

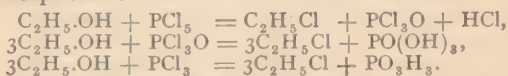


The transposition is brought about by heating the alcohol previously saturated with the halogen hydride :—



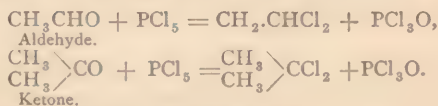
This rearrangement between the two reacting compounds is, however, not complete. It depends very much on the mass of the substances reacting, and upon the temperature (compare esters of mineral and fatty acids). The alteration is most speedy with HI ; however, transpositions sometimes occur in this case, in the higher alcohols. See p. 67.

The change is most complete when effected by the halogen products of phosphorus :—



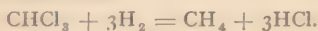
Even here the reaction is not perfect. Phosphoric and phosphorous acids are formed, and these convert a portion of the alcohol into ethereal salts, which constitute the residue after distilling off the halogen derivatives.

(5) By the action of  $\text{PCl}_3$  and  $\text{PBr}_3$  upon the aldehydes and ketones, when an atom of oxygen is replaced by two halogen atoms :—



The halogen derivatives prepared according to these methods are partly identical, as will be seen further on, and partly isomeric. They are generally colorless, ethereal smelling liquids, *insoluble* in water. The iodides redden in sunlight, iodine separating. The chlorides and bromides burn with a green-edged flame.

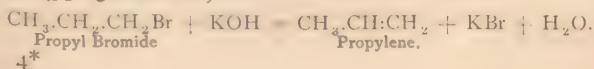
Nascent hydrogen (zinc and hydrochloric acid or glacial acetic acid, sodium amalgam and water) can reconvert all the halogen derivatives, by successive removal of the halogen atoms, into the corresponding hydrocarbons :



When the mono-halogen compounds are heated with moist silver oxide, the corresponding alcohols are produced :—



Alcoholic sodium and potassium hydrates occasion the splitting off of a halogen hydride, and the production of unsaturated compounds : (pp. 54 and 61) :—





In this reaction the halogen attracts to itself the hydrogen of the least hydrogenized adjacent carbon atom (compare p. 64). Such a splitting sometimes occurs on application of heat, and it appears that the primary alkylogens are more easily decomposed than the secondary and tertiary (see p. 67).

# (1) HALOGEN COMPOUNDS— $C_nH_{2n+1}X$ .

## ALKYLOGENS.

Because of their formation from the alcohols by the action of the halogen hydrides, the alkylogens are called *haloid esters*. They are perfectly analogous to the true esters produced by the action of alcohols and oxygen acids.

**Monochlormethane**,  $CH_3Cl$ , **Methyl chloride**, is obtained from methane or methyl alcohol. At ordinary temperatures it is a gas, that may be condensed to a liquid (by a freezing mixture of ice and calcium chloride). It boils at  $-22^\circ$ . Alcohol will dissolve 35 volumes of it, and water 4 volumes.

It is prepared by heating a mixture of 1 part methyl alcohol (wood spirit), 2 parts sodium chloride, and 3 parts sulphuric acid. A better plan is to conduct HCl into boiling methyl alcohol in the presence of zinc chloride ( $\frac{1}{2}$  part). The disengaged gas is washed with KOH, and dried by means of sulphuric acid. The commercial methyl chloride occurring in compressed condition and finding application in the manufacture of the aniline dyes and the production of cold is obtained by heating trimethylamine hydrochloride  $N(CH_3)_3 \cdot HCl$ .

**Monochlorethane**,  $C_2H_5Cl$ , **Ethyl chloride**, is an ethereal liquid, boiling at  $12.5^\circ$ ; specific gravity at  $0^\circ = 0.921$ . It is miscible with alcohol, but is slightly soluble in water.

*Preparation.*—Heat a mixture of 1 part ethyl alcohol, 2 parts  $H_2SO_4$ , and 2 parts NaCl. The gas is washed by passing through warm water and condensed in a strongly cooled receiver. Or HCl may be passed into 95 per cent. alcohol containing  $\frac{1}{2}$  part  $ZnCl_2$ . Heat should be applied.

If heated with water to  $100^\circ$  (in a sealed tube), it changes to ethyl alcohol. The conversion is more rapid with potassium hydroxide. In dispersed sunlight, chlorine acts upon it to form ethylidene chloride  $CH_3 \cdot CHCl_2$  and substitution products. Of these  $C_2HCl_3$  was formerly employed as *Aether anæstheticus*.

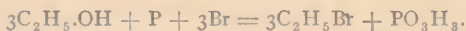
**Monochloropropane**,  $C_3H_7Cl$ . Two isomerides are possible:—

Normal propyl chloride,  $CH_3 \cdot CH_2 \cdot CH_2 \cdot Cl$ , derived from normal propyl alcohol, boils at  $46.5^\circ$ . Its specific gravity is 0.8898 at  $0^\circ$ .

Isopropyl chloride,  $CH_3 \cdot CHCl \cdot CH_3$ , obtained from the corresponding alcohol, and by the union of propylene with HCl, boils at  $37^\circ$ ; its specific gravity is 0.874 at  $10^\circ$ .

**Monochlor-Butanes**,  $C_4H_9Cl$ , Butyl chlorides. Four isomerides are possible: two of these arise from the normal and two from the tertiary butane (see p. 49). These (and also their homologues), will be mentioned under the corresponding alcohols.

For the preparation of the bromides from alcohols, the already made  $\text{PBr}_5$  (or  $\text{PCl}_3\text{Br}$ ) (see p. 65) is not essential. Amorphous phosphorus is taken, alcohol poured over it, and while carefully cooling, bromine is gradually added. The mixture is subsequently distilled :—



The distillate is washed with  $\text{H}_2\text{O}$  and dilute  $\text{KOH}$ , dried over  $\text{CaCl}_2$ , and then fractionated. The bromides boil from  $22\text{--}24^\circ$  higher than their corresponding chlorides.

The bromides may be obtained from the chlorides, by heating with aluminium bromide (*Berichte*, 14, 1709) :—



Conversely, the bromides are changed to chlorides through the agency of  $\text{HgCl}_2$ .

**Methyl Bromide**,  $\text{CH}_3\text{Br}$ —Monobrommethane—boils at  $+4.5^\circ$ ; its specific gravity is 1.73 at  $0^\circ$ .

**Ethyl Bromide**,  $\text{C}_2\text{H}_5\text{Br}$ , boils at  $39^\circ$ ; its specific gravity is 1.47 at  $13^\circ$ . Ethylidene Bromide,  $\text{CH}_3\text{CHBr}_2$ , and ethylene bromide,  $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br}$ , are obtained from it by the action of bromine.

**Propyl Bromide**,  $\text{C}_3\text{H}_7\text{Br}$ , from the normal alcohol, boils at  $71^\circ$ ; its specific gravity is 1.3520 at  $20^\circ$ .

**Isopropyl Bromide**,  $\text{C}_3\text{H}_7\text{Br}$ , from its corresponding alcohol, boils at  $60\text{--}63^\circ$ ; its specific gravity is 1.3097 at  $20^\circ$ . It is most conveniently obtained by the action of bromine upon isopropyl iodide (*Berichte* 15, 1904).

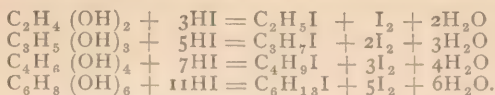
Upon boiling with aluminium bromide or by heating to  $250^\circ$ , normal propyl bromide passes over into the isopropyl bromide (not completely, however, *Berichte* 16, 391.). Such a transposition, due to displacement of the atoms in the molecule, occurs rather frequently, and is termed *molecular transposition*. In many instances it may be explained by the formation of intermediate products. Thus, it may be assumed that the normal propyl bromide at first breaks up into propylene  $\text{CH}_3\cdot\text{CH}:\text{CH}_2$  and  $\text{HBr}$  (see p. 65) which then, according to a common rule of addition, (p. 64) unites with the propylene to isopropyl bromide,  $\text{CH}_3\cdot\text{CHBr}\cdot\text{CH}_2$ . Similarly, isobutyl bromide  $(\text{CH}_3)_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{Br}$  changes at  $240^\circ$  to tertiary butyl bromide  $(\text{CH}_3)_3\cdot\text{CBr}\cdot\text{CH}_3$ . The transpositions occurring on heating the halogen hydrides with the alcohols may be explained in the same manner.

The iodides are obtained just like the bromides, that is, by heating a mixture of the alcohols, phosphorus (yellow or amorphous) and iodine. Concentrated  $\text{HI}$  converts the alcohols into iodides :—



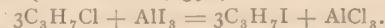
Excess of  $\text{HI}$ , however, again reduces them. (Compare p. 64).

The polyatomic alcohols (containing several hydroxyl groups) also yield mono-iodides:—



The mechanism of the reaction will be more carefully studied when we reach allyl and isopropyl iodides.

Many iodides can be obtained from the chlorides by heating with  $\text{AlI}_3$  or  $\text{CaI}_2$  (*Berichte* 16, 392):—



In some cases HI accomplishes the same. Conversely the iodides can be changed to chlorides by heating with mercuric or stannic chlorides:—



Free chlorine and bromine can also replace iodine directly:—



On exposure to the air the iodides soon become discolored by deposition of iodine. The iodides of the secondary and tertiary alcohols are easily converted by heat into alkylens  $\text{C}_n\text{H}_{2n}$  and HI. Their boiling points are about  $33^\circ$  higher than those of the corresponding bromides.

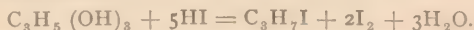
**Methyl Iodide**,  $\text{CH}_3\text{I}$ , is a heavy, sweet-smelling liquid, boiling at  $45^\circ$ , and has a sp. gr. = 2.19 at  $0^\circ$ . In the cold it unites with  $\text{H}_2\text{O}$  to form a crystalline hydrate  $\text{CH}_3\text{I} + \text{H}_2\text{O}$ .

**Ethyl Iodide**,  $\text{C}_2\text{H}_5\text{I}$ , is a colorless, strongly refracting liquid, boiling at  $72^\circ$  and having a sp. gr. of 1.975 at  $0^\circ$ .

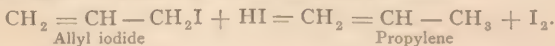
*Preparation.*—Pour 5 parts (90 per cent.) alcohol over 1 part amorphous phosphorus, then gradually add 10 parts iodine and distil. The distillate is poured back on the residue and redistilled. It is advisable to previously dissolve the iodine in alcohol or ethyl iodide, and add this to the alcohol containing phosphorus. In this case yellow phosphorus may be employed.

**Propyl Iodide**,  $\text{C}_3\text{H}_7\text{I}$ , boils at  $102^\circ$ , and has a specific gravity of 1.7427 at  $20^\circ$ .

**Isopropyl Iodide**,  $\text{C}_3\text{H}_7\text{I}$ , is formed from isopropyl alcohol, propylene glycol  $\text{C}_3\text{H}_6(\text{OH})_2$ , or from propylene, and is most conveniently prepared by distilling a mixture of glycerol, amorphous phosphorus and iodine:



Here we have allyl iodide produced first (see p. 71), and this is further changed to propylene and isopropyl iodide:—



and



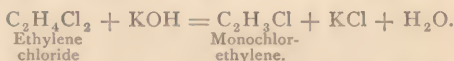
*Preparation*.—300 gr. iodine and 200 gr. glycerol (diluted with an equal volume of  $H_2O$ ) are placed in a tubulated retort, and 55 gr. of yellow phosphorus added gradually. The portion passing over first is returned and redistilled. To remove admixed allyl iodide from the isopropyl iodide, conduct it into  $HI$  and let stand. (*Annalen*, 138, 364.)

Isopropyl iodide boils at  $89.9^\circ$ , and has a specific gravity of 1.7033 at  $20^\circ$ .

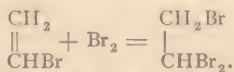
The higher alkyl iodides are mentioned under the corresponding alcohols.

HALOGEN DERIVATIVES— $C_nH_{2n-1}X$  and  $C_nH_{2n-2}X_2$ .

As a general thing, the halogen substitution products of the unsaturated hydrocarbons cannot be prepared by direct action of the halogens, since addition products are apt to result (p. 55). They are produced, however, by the moderated action of alcoholic potash or  $Ag_2O$  upon the substituted hydrocarbons  $C_nH_{2n}X_2$ . This reaction occurs very readily if we employ the addition products of the olefines:—



If the alcoholic potash acts very energetically the hydrocarbons of the acetylene series are formed (p. 60). Being unsaturated compounds they unite directly with the halogens, and also the hydrides of the latter:—

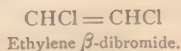
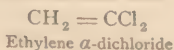


**Monochlorethylene**,  $C_2H_3Cl = CH_2:CHCl$ , or Vinyl chloride (the group  $CH_2:CH$  is called Vinyl), derived from ethylene chloride,  $CH_2Cl.CH_2Cl$ , and (although with greater difficulty) from ethylenide chloride,  $CH_3.CHCl_2$ , is a gas with garlic like smell, liquefying at  $-18^\circ$  and polymerizing in the sunlight.

**Monobromethylene**,  $C_2H_3Br$ , Vinyl bromide, is obtained by boiling ethylene bromide with aqueous potassium hydrate. It possesses an odor similar to that of the chloride, boils at  $16^\circ$ , and has a specific gravity of 1.52. Under certain conditions, in sunlight, for example, it is converted into a solid polymeric modification. It dissolves readily in concentrated sulphuric acid, and if the solution be boiled with water croton aldehyde results (from acetaldehyde that is formed previously). Vinyl bromide does not react with  $CNAg$  or  $CNK$ , and, indeed, does not appear capable of double decompositions. (*Berichte*, 14, 1532.)

**Ethylene Mono-iodide**,  $C_2H_3I$ , Vinyl iodide, is obtained from ethylene and ethylenide iodides, by the aid of alcoholic potash, and boils at  $55^\circ$ ; its specific gravity is 1.98.

**Ethylene Dichlorides and Dibromides**:—



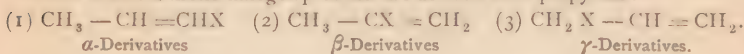
**Ethylene  $\alpha$ -Dichloride** (unsymmetrical), is formed from ethylene chloride,  $CH_2Cl.CHCl_2$ , by the action of alcoholic potash, and boils at  $37^\circ$ . **Ethylene  $\beta$ -dichloride** (symmetrical) is formed by the union of acetylene,  $C_2H_2$ , with



$\text{SbCl}_5$ . It boils at  $55^\circ$ . **Ethylene  $\alpha$ -Dibromide**, from bromethylene bromide,  $\text{CH}_2\text{Br}.\text{CHBr}_2$ , boils at  $91^\circ$ . **Ethylene  $\beta$ -dibromide**, formed from acetylene by addition of  $\text{Br}_2$ , and from acetylene tetrabromide,  $\text{C}_2\text{H}_2\text{Br}_4$  through the agency of zinc, boils at  $110^\circ$ . Ethylene  $\alpha$ -dibromide, with benzene and  $\text{AlCl}_3$ , yields ethylene diphenyl,  $\text{CH}_2:\text{C}(\text{C}_6\text{H}_5)_2$ ; but from ethylene  $\beta$ -dibromide dibenzyl is obtained,  $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}_2.\text{C}_6\text{H}_5$ . (*Berichte*, 16, 622.)

The unsymmetrical products are inclined to polymerize. This is not the case with the symmetrical (*Berichte*, 12, 2076). The ethylene mono-haloids polymerize similarly, but ethylene itself does not change. It appears, too, that the power of direct union with oxygen, affording the chloranhydrides of substituted acetic acids, is only possessed by the unsymmetrical substitution products (*Berichte*, 13, 1980, 16, 2918).

Three different mono-halogen products are derived from propylene:—



(1) The  $\alpha$  derivatives are obtained from the propylidene compounds,  $\text{CH}_3.\text{CHX}_2$  (from propyl aldehyde), when the latter are heated with alcoholic potassium hydrate, while from the addition products of propylene,  $\text{CH}_3.\text{CHBr}.\text{CH}_2.\text{Br}$ , we obtain the  $\beta$ -derivatives at the same time. Propylene  $\alpha$ -chloride boils at  $35^\circ$ ,  $\alpha$ -Bromopropylene boils at  $59\text{--}60^\circ$ ; its specific gravity at  $19^\circ$  is 1.428.

(2) The  $\beta$ -derivatives,  $\text{CH}_3.\text{CX}:\text{CH}_2$ , are prepared in pure condition from the halogen compounds derived from acetone. Propylene  $\beta$ -chloride boils at  $23^\circ$ ; its sp. gr. at  $9^\circ$  is 0.918. Propylene  $\beta$ -bromide boils at  $48^\circ$ ; its sp. gr. at  $19^\circ$  is 1.364.

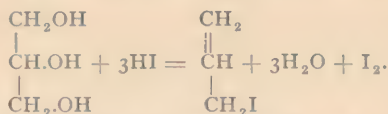
Continued heating with alcoholic potash causes both  $\alpha$ - and  $\beta$ -varieties to pass into allylene. Propylene  $\beta$ -bromide combines in the cold with  $\text{HBr}$  to form acetal bromide,  $\text{CH}_3.\text{CBr}_2.\text{CH}_3$ , while the  $\alpha$  variety only unites with it at  $100^\circ$ , and then yields a mixture of propylene and propylidene bromide (p. 73). Sulphuric acid and water, aided by heat, convert the  $\beta$ -chloride into acetone,  $\text{CH}_3.\text{CO}.\text{CH}_3$ . The  $\alpha$ -products especially appear to react with far more difficulty (like ethylene monochloride) than the  $\beta$ -varieties (compare the chlorides of styrolene).

(3) The  $\gamma$ -derivatives of propylene  $\text{CH}_2\text{X} - \text{CH} = \text{CH}_2$  are designated *Allyl haloids*, because they correspond to allyl alcohol,  $\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}$ . The so-called allyl group ( $\text{CH}_2:\text{CH}.\text{CH}_2$ ), occurs in some vegetable substances (mustard oil, oil of garlic). Heated with alcoholic potash the allyl haloids yield allyl ethyl ether,  $\text{C}_3\text{H}_5.\text{O}.\text{C}_2\text{H}_5$ . That which chiefly distinguishes them from the  $\alpha$ - and  $\beta$ -products is their capability of readily undergoing transpositions.

**Allyl chloride**,  $\text{C}_3\text{H}_5\text{Cl}$ , is formed by the action of  $\text{PCl}_3$  or  $\text{HCl}$  upon allyl alcohol, or by the transposition taking place between allyl iodide and  $\text{HgCl}_2$  (p. 68). It is a liquid with an odor resembling that of leeks; boils at  $46^\circ$ , and has a specific gravity of 0.9379 at  $20^\circ$ . If heated to  $100^\circ$  with concentrated hydrochloric acid it affords propylene chloride,  $\text{CH}_3.\text{CHCl}.\text{CH}_2\text{Cl}$  (Trimethylene chloride,  $\text{CH}_2\text{Cl}.\text{CH}_2.\text{CH}_2\text{Cl}$ , is not produced).

**Allyl Bromide**,  $C_3H_5Br$ , boils at  $70.71^\circ$ ; its specific gravity at  $0^\circ$  equals 1.461. Upon warming to  $100^\circ C$ . it combines with concentrated  $HBr$  to form  $CH_2Br.CH_2.CH_2Br$  (see p. 74).

**Allyl Iodide**,  $C_3H_5I$ , is obtained from allyl alcohol, or better, from glycerol, by the action of  $HI$  or iodine and phosphorus (compare p. 68):—



We may suppose that at first  $CH_2I.CHI.CH_2I$  forms and is subsequently decomposed into  $CH_2:CH.CH_2I$  and  $I_2$ . With excess of  $HI$  or phosphorus iodide, allyl iodide is further converted into propylene and isopropyl iodide (p. 68).

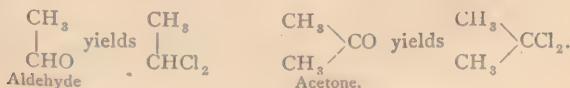
*Preparation.*—150 parts of concentrated glycerol and 100 parts pulverized iodine are introduced into a tubulated retort, and 60 parts of yellow phosphorus gradually added to the mixture. When the first action has passed away, the allyl iodide is distilled off and the distillate washed with dilute potassium hydrate. When larger quantities are employed explosions sometimes occur; these may be obviated if the operation be carried out in a stream of  $CO_2$  gas. (Compare *Annalen* 185, 191.)

Allyl iodide is a colorless liquid, with a leek-like odor, boiling at  $101^\circ$ . Its specific gravity equals 1.789 at  $16^\circ$ . By continued shaking of allyl iodide (in alcoholic solution) with mercury,  $C_3H_5HgI$  separates in colorless leaflets (see mercury ethyl). Iodine liberates pure allyl iodide from this:—

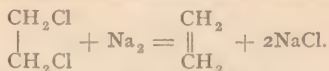


### DIHALOGEN COMPOUNDS $C_nH_{2n}X_2$ .

These derivatives of the paraffins arise by direct substitution, by the addition of halogens to the alkylens  $C_nH_{2n}$ , and the halogen hydrides to the substituted alkylens  $C_nH_{2n-1}X$ ; and by the action of the phosphorus haloids upon the aldehydes and ketones (p. 65). The products thus obtained are of like composition, and are partly identical, partly isomeric. The direct addition products  $C_nH_{2n}X_2$  have the halogen atoms attached to two adjacent carbon atoms (see p. 55). In the compounds resulting from the replacement of the oxygen of aldehydes and ketones, both halogen atoms are in union with the same carbon atom:—



Heated with alcoholic potash, the addition products pass into the compounds  $C_n H_{2n-1} X$  and  $C_n H_{2n-2}$  (page 60). The alkylens result when the dihalogen compounds are heated with sodium:—



Those derivatives, in which the halogens are attached to different carbon atoms, are capable of forming glycols:—



**Methylene Chloride, Dichlormethane,  $\text{CH}_2\text{Cl}_2$ ,** is produced in the chlorination of  $\text{CH}_3\text{Cl}$ , by the action of  $\text{Cl}$  upon  $\text{CH}_2\text{I}_2$  or  $\text{CH}_3\text{I}$ , and by the reduction of chloroform by means of zinc and ammonia. It is a colorless liquid, boiling at  $41^\circ$ , and having a specific gravity of 1.36 at  $0^\circ$ .

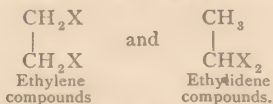
**Methylene Bromide,  $\text{CH}_2\text{Br}_2$ ,** results on heating  $\text{CH}_3\text{Br}$  with bromine (together with  $\text{CHBr}_3$ ) and also by the action of bromine upon methylene iodide. It boils at  $81^\circ$  ( $98.5^\circ$ ) and has a specific gravity of 2.493 at  $0^\circ$ .

**Methylene Iodide,  $\text{CH}_2\text{I}_2$ ,** is produced in the action of sodium alcoholate upon iodoform,  $\text{CHI}_3$ , and is best prepared by heating  $\text{CHCl}_3$  or  $\text{CHI}_3$  with fuming  $\text{HI}$  to  $130^\circ$ :—



Colorless, shining leaflets, fusing at  $+4^\circ$  (specific gravity 3.34), and boiling about  $182^\circ$  with partial decomposition.

The empirical formula  $C_2H_4X_2$  has two possible structures:—



The first originate from ethylene, the second from aldehyde  $\text{CH}_3\text{.COH}$  (p. 71). The former yield acetylene with alcoholic potash, the latter acetal,  $\text{CH}_3\text{.CH} \begin{array}{l} \text{O.C}_2\text{H}_5 \\ \text{O.C}_2\text{H}_5 \end{array}$ ; the former yield glycol, the latter do not.

**Ethylene chloride,  $C_2H_4\text{Cl}_2$ ,** is obtained by the direct union of equal volumes of ethylene and chlorine gas, or by conducting ethylene through warm  $\text{SbCl}_5$ . It is a colorless, pleasant-smelling liquid, of specific gravity 1.2521 at  $20^\circ$ , and boils at  $84^\circ$ .

**Ethylidene Chloride,  $\text{CH}_3\text{.CHCl}_2$ ,** is produced by the chlorination of ethyl chloride (both gases are conducted over animal charcoal heated to about  $300^\circ$ ) and from aldehyde (better paraldehyde) by the action of  $\text{PCl}_5$ . On a large scale it appears as a by-product in the preparation of chloral. It is a liquid, smelling like

chloroform, with a specific gravity of 1.1743 at 20°, boils at 57.7°, and is employed as an anæsthetic. By further chlorination it yields  $\text{CH}_3\text{CCl}_3$  together with a little  $\text{CH}_2\text{Cl}\cdot\text{CHCl}_2$ . When  $\text{AlCl}_3$  is present, the latter is the only product.

**Ethylene Bromide**,  $\text{C}_2\text{H}_4\text{Br}_2$ , is formed by saturating bromine with ethylene gas (*Annalen*, 192, 244), and is an oily, pleasant-smelling liquid, boiling at 131°; its specific gravity is 2.178 at 20°. At 0° it solidifies to a crystalline mass, fusing at + 9°.

**Ethylidene Bromide**,  $\text{C}_2\text{H}_4\text{Br}_2 = \text{CH}_3\cdot\text{CHBr}_2$ , formed together with ethylene bromide by the bromination of  $\text{C}_2\text{H}_5\text{Br}$  (in presence of  $\text{AlBr}_3$ , only ethylene bromide is produced), is obtained by the action of  $\text{PCl}_3\text{Br}_2$  upon aldehyde. It boils at 110.5°, and has a specific gravity of 2.082 at 21°.

The formation of ethylene and ethylidene-bromides from monobromethylene is quite interesting. When the latter is heated with very concentrated  $\text{HBr}$ , ethylene-bromide forms, while with more dilute acid ethylidene-bromide results.

**Ethylene Iodide**,  $\text{C}_2\text{H}_4\text{I}_2$ , is produced in the union of iodine with ethylene, by conducting the latter into a solution of iodine in alcohol. It crystallizes from alcohol in brilliant needles, which rapidly become yellow on exposure to light. The compound melts at 81°, and at higher temperatures decomposes into  $\text{C}_2\text{H}_4$  and  $\text{I}_2$ . It may be distilled in an atmosphere of ethylene gas without decomposition.

**Ethylidene Iodide**,  $\text{C}_2\text{H}_5\text{CHI}_2$ , is obtained from ethylidene chloride by the action of aluminium iodide (p. 68). It boils at 178°, sustaining partial decomposition; its specific gravity is 2.84 at 0°. It also forms by the addition of  $2\text{HI}$  to acetylene.

Four different di-halogen products are derived from propane  $\text{C}_3\text{H}_8$ :—

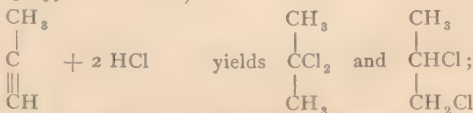
(1) Derivatives of the first structure, called propylidene compounds, arise from propyl aldehyde  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CHO}$  by the action of  $\text{PCl}_5$ .

**Propylidene Chloride**,  $\text{C}_3\text{H}_6\text{Cl}_2$ , is a liquid, with an odor resembling that of leeks, and boiling at 84-87°. Its specific gravity at 10° is 1.143. The bromide,  $\text{C}_3\text{H}_6\text{Br}_2$ , from propylene  $\alpha$ -bromide, boils at 130°.

(2) Derivatives of the formula  $\text{CH}_3\cdot\text{CX}_2\cdot\text{CH}_3$  are obtained from acetone by the action of  $\text{PCl}_5$  and  $\text{PBr}_5$ :



**Dimethyl Methylene Chloride**,  $\text{C}_3\text{H}_6\text{Cl}_2 = \text{CH}_3\cdot\text{CCl}_2\cdot\text{CH}_3$ , methyl chlor acetol or acetone chloride, is formed by the addition of  $2\text{HCl}$  to allylene (together with propylene chloride):



and by the chlorination of isopropyl chloride  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_3$ .



It is a colorless liquid, boiling at  $69-70^{\circ}$ , and having a specific gravity 1.827 at  $16^{\circ}$ .  $\beta$ -Monochloropropylene is obtained from it by action of alcoholic potash (p. 70). Heated to  $150^{\circ}$  with water, it changes in part to acetone.

**Dimethyl Methylene Bromide**,  $C_3H_6Br_2$ , from acetone (p. 71) and from allylene, by the addition of 2 HBr, boils at  $113-116^{\circ}$ ; its specific gravity at  $0^{\circ}$  is 1.875.

(3) We get the derivatives of the structure  $CH_3.CHX.CH_2X$  by uniting propylene with the halogens:



This class passes into propylene glycol when acted upon by moist silver oxide; with alcoholic potash they yield  $CH_3.CX.CH_2$ , and allylene.

**Propylene Chloride**,  $C_3H_6Cl_2 = CH_3.CHCl.CH_2Cl$ , is produced, together with acetone chloride, when chlorine acts in sunlight upon isopropyl-chloride (in presence of iodine the chlorination extends only to propylene chloride). It boils at  $97^{\circ}$ , and has a specific gravity of 1.165 at  $14^{\circ}$ .

**Propylene Bromide**,  $C_3H_6Br_2 = CH_3.CHBr.CH_2Br$ , is a liquid boiling at  $141^{\circ}$ . It is formed in the bromination of propyl bromide and isopropyl bromide. Its specific gravity at  $17^{\circ}$  equals 1.946. Propionic aldehyde and acetone result when propylene bromide or the chloride is heated, together with  $H_2O$ , to  $200^{\circ}$ .

**Propylene Iodide**,  $C_3H_6I_2 = CH_3.CHI.CH_2I$ , results by the union of iodine with propylene at  $50^{\circ}$ . It is a colorless oil, that cannot be distilled without suffering decomposition.

(4) The products of the formula  $CH_2X.CH_2.CH_2Cl$  are designated trimethylene derivatives.

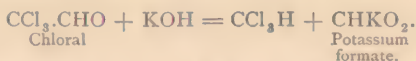
**Trimethylene Chloride**,  $C_3H_6Cl_2 = CH_2Cl.CH_2.CH_2Cl$ , is obtained by heating the corresponding bromide with mercuric chloride to  $160^{\circ}$ . It is an agreeably smelling liquid, that boils at  $119^{\circ}$ , and at  $15^{\circ}$  has a sp. gr. = 1.201.

**Trimethylene Bromide**,  $C_3H_6Br_2$ , results on heating allyl bromide  $CH_2:CH.CH_2Br$  with concentrated hydrobromic acid. Propylene bromide is produced at the same time. This can be removed by fractional distillation. (With HCl the only product of allyl chloride is propylene chloride  $CH_3.CHCl.CH_2Cl$ .) It is obtained in a purer form on saturating allyl bromide with HBr in the cold, and letting the whole stand some time (*Annalen* 197, 184). Trimethylene bromide is a colorless liquid, boiling at  $164^{\circ}$ , and has a specific gravity of 2.01 at  $0^{\circ}$ . When treated with alcoholic potash, it yields allyl bromide and allyl ethyl ether. Trimethylene is the product with sodium (p. 58). Continued boiling with water converts it into trimethylene glycol.

#### THE HALOGEN COMPOUNDS $C_nH_{2n-1}X_3$ .

**Chloroform**,  $CHCl_3$ , Trichlormethane, is formed: by the chlorination of  $CH_4$  or  $CH_3Cl$ ; by the action of chloride of lime upon different carbon compounds, *e. g.*, methyl or ethyl alcohol,

acetone, acetic acid; and by heating chloral with aqueous potassium or sodium hydrate:



In preparing chloroform a mixture of alcohol, bleaching lime and water is distilled from a capacious retort (*Annalen* 165, 349). The chloroform produced is carried over with the steam and collects in the bottom of the receiver as a heavy oil. It is purified by shaking with  $\text{H}_2\text{SO}_4$  and repeated distillation. At present it is generally obtained from chloral. Pure chloroform should not color on addition of concentrated sulphuric acid.

Chloroform is a colorless liquid of an agreeable ethereal odor and sweetish taste. It boils at  $61^\circ$ , and its specific gravity at  $0^\circ$  equals 1.526. Inhalation of its vapors causes unconsciousness, and at the same time has an anæsthetic effect. It is uninflammable. Chlorine changes it to  $\text{CCl}_4$ . Potassium formate is produced when chloroform is heated with alcoholic potash:—



The so-called tribasic formic acid ester  $\text{CH}(\text{O.C}_2\text{H}_5)_3$ , is produced by treating with sodium alcoholate. When heated to  $180^\circ$  with aqueous or alcoholic ammonia, it forms ammonium cyanate and chloride. When  $\text{KOH}$  is present, an energetic reaction takes place at ordinary temperatures. The equation is:—



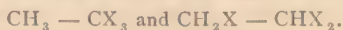
**Bromoform**,  $\text{CHBr}_3$ , is produced in the same way as chloroform, by the action of bromine and  $\text{KOH}$  upon methyl and ethyl alcohol. It is a colorless, agreeable-smelling liquid, solidifying at  $-9^\circ$ . It boils at  $151^\circ$  and has a specific gravity 2.83 at  $0^\circ$ .

**Iodoform**,  $\text{CHI}_3$ . When iodine and potash act upon ethyl alcohol, or acetone, aldehyde and other substances containing the methyl group, this compound results. Pure methyl alcohol, however, does not yield iodoform. (*Berichte*, 13, 1002).

*Preparation*.—Dissolve 2 parts crystallized soda in 10 parts of water, add 1 part alcohol, bring the whole to  $60$ – $80^\circ$ , and gradually introduce the 1 part of iodine. The iodoform that separates is filtered off. By renewed warming of the filtrate with  $\text{KOH}$  and alcohol, followed by the introduction of chlorine, an additional quantity of iodoform may be obtained.

Iodoform crystallizes in brilliant, yellow leaflets, soluble in alcohol and ether. Its odor is saffron-like. It evaporates at medium temperatures; fuses at  $119^\circ$  and distils over with the aqueous vapor. Digested with alcoholic  $\text{KOH}$ , or  $\text{HI}$ , it passes into methylene iodide,  $\text{CH}_2\text{I}_2$ .

Two isomeric tri-halogen derivatives may be obtained from ethane  $\text{C}_2\text{H}_6$ :—



**$\alpha$ -Trichlor-Ethane**,  $\text{CH}_3.\text{CCl}_3$ , is produced (together with  $\text{CH}_2\text{Cl}.\text{CHCl}_2$ ) by the chlorination of ethyl and ethylidene chloride in sunlight. It is a liquid with chloroform-like odor, and boils at  $74.1^\circ$ . Its specific gravity at  $0^\circ$  is 1.346. If heated with KOH it yields potassium acetate:—



Treated with sodium alcoholate it affords the tri-ethyl ester  $\text{CH}_3.\text{C}(\text{O}.\text{C}_2\text{H}_5)_3$ . Further chlorination of trichlor-ethane produces  $\text{CH}_2\text{Cl}.\text{CCl}_3$ , boiling at  $131^\circ$ ,  $\text{CHCl}_2.\text{CCl}_3$  at  $162^\circ$ , and perchlor-ethane  $\text{CCl}_3.\text{CCl}_3$  (see p. 77).  $\text{CHCl}_2.\text{CHCl}_2$ , from dichlor-aldehyde, boils at  $113.7^\circ$  (*Berichte*, 15, 2563).

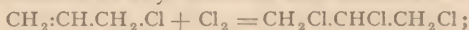
**$\beta$ -Trichlor-Ethane**,  $\text{CH}_2\text{Cl}.\text{CHCl}_2$ , monochlor-ethylene chloride, is produced by the union of vinyl chloride  $\text{CH}_2.\text{CHCl}$  with  $\text{Cl}_2$ , and boils at  $113.7^\circ$ . Its specific gravity at  $0^\circ$  equals 1.422.

**$\alpha$ -Tribrom-Ethane**,  $\text{CH}_3.\text{CBr}_3$ , has not been formed.

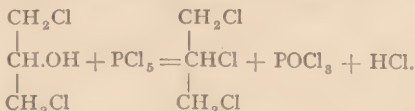
**$\beta$ -Tribrom-Ethane**,  $\text{CH}_2\text{CHBr}_2$ , monobrom-ethylene bromide, forms upon brominating ethyl and ethylene bromides, also by addition of bromine to brom-ethylene,  $\text{CH}_2.\text{CHBr}$ . It boils at  $187^\circ$ ; its specific gravity at  $21^\circ$  equals 2.610.

Trisubstituted propane  $\text{C}_3\text{H}_5\text{X}_3$ , can have five structural forms.

The most important derivatives are those having the formula  $\text{CH}_2\text{X}.\text{CHX}.\text{CH}_2\text{X}$ . They correspond to glycerol  $\text{CH}_2(\text{OH}).\text{CH}(\text{OH}).\text{CH}_2(\text{OH})$ . The trivalent group  $\text{CH}_2.\text{CH}.\text{CH}_2$ , present in them, is termed *glyceryl*. They are produced by the addition of chlorine or bromine to allyl chloride and bromide:—



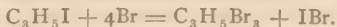
or by the action of  $\text{PCl}_5$  upon dichlorhydrin, which is derived from glycerol:—



Moist silver oxide converts them into glycerol.

**Glyceryl Chloride**,  $\text{C}_3\text{H}_5\text{Cl}_3$ , allyl trichloride, trichlorhydrin, is a liquid with an odor resembling chloroform, and boiling at  $158^\circ$ . Its specific gravity at  $15^\circ$  equals 1.417.

**Glyceryl Bromide**,  $\text{C}_3\text{H}_5\text{Br}_3$ , tribromhydrin, is best obtained by the action of bromine upon allyl iodide:



It crystallizes in colorless, shining leaflets, fusing at  $16^\circ$ , and boiling at  $220^\circ$ .

**Glyceryl Iodide**,  $\text{C}_3\text{H}_5\text{I}_3$ , appears not to exist. It decomposes at once into allyl iodide and  $\text{I}_2$  (p. 71).

Among the higher substitution products may be mentioned the following carbon haloids:—

**Tetrachlor-methane** or **Carbon Tetrachloride**,  $\text{CCl}_4$ , is

formed by the action of chlorine upon chloroform, and by conducting a mixture of  $\text{Cl}$  and  $\text{CS}_2$  through tubes heated to redness.

*Preparation.* Chlorine is conducted through boiling chloroform exposed to sunlight, or through a mixture of  $\text{CS}_2$  and  $\text{SbCl}_5$ . In the latter case, sulphur chloride is formed at the same time. This may be decomposed by shaking with  $\text{KOH}$ .

A pleasant-smelling liquid, boiling at  $76-77^\circ$ . Its specific gravity is 1.631 at  $0^\circ$ . At  $30^\circ$  it solidifies to a crystalline mass. Heated with alcoholic  $\text{KOH}$ , it decomposes according to the following equation:—



When the vapors are conducted through a red hot tube, decomposition occurs, and  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{Cl}_6$  are produced.

**Tetrabrommethane**,  $\text{CBr}_4$ , obtained by the action of brom-iodide upon bromoform or  $\text{CS}_2$ , crystallizes in shining plates, melting at  $92.5^\circ$ , and boiling, with but little decomposition, at  $189^\circ$ .

**Tetraiodomethane**,  $\text{CI}_4$ , carbon iodide, is formed when  $\text{CCl}_4$  is heated with aluminium iodide (p. 68). It crystallizes from ether in dark red, regular octahedra, of specific gravity 4.32 at  $20^\circ$ . On exposure to air it decomposes into  $\text{CO}_2$  and  $\text{I}$ . Heat accelerates the decomposition.

**Perchlorethane**,  $\text{C}_2\text{Cl}_6$ , is the final product in the action of  $\text{Cl}$  upon  $\text{C}_2\text{H}_5\text{Cl}$  or  $\text{C}_2\text{H}_4\text{Cl}_2$ . It is a crystalline mass, with a camphor-like odor and specific gravity 2.01. It melts at  $187-188^\circ$ . At ordinary temperatures it vaporizes without fusing, as its critical pressure (compare Inorganic Chemistry), lies above 760 mm. It boils at  $185^\circ.5$  under a pressure of 776.7 mm. It is readily soluble in alcohol and ether. When its vapors are conducted through tubes heated to redness, it breaks up into  $\text{Cl}_2$  and ethylene perchloride,  $\text{C}_2\text{Cl}_4$ . This is a mobile liquid, boiling at  $121^\circ$ . Its specific gravity at  $20^\circ$  is 1.6226.

**Perbrommethane**,  $\text{C}_2\text{Br}_6$ , is a colorless crystalline compound, difficultly soluble in alcohol and ether. At  $200^\circ$  it decomposes into  $\text{Br}_2$  and ethylene perbromide  $\text{C}_2\text{Br}_4$ , which consists of colorless crystals, melting at  $53^\circ$ .

**Perchlormesole**,  $\text{C}_4\text{Cl}_6$ , is formed on heating hexyl iodide or amyl chloride with  $\text{ICl}_3$ . It melts at  $39^\circ$ , and boils at  $284^\circ$  (*Berichte*, 10, 804).

## NITRO-DERIVATIVES OF THE HYDROCARBONS.

By this designation is understood compounds of carbon in which the hydrogen combined with the latter is replaced by the monovalent nitro-group,  $\text{NO}_2$ . The carbon is directly united to the nitrogen by one affinity. An universal method for the production of nitro-compounds consists in acting upon the hydrocarbon derivatives with concentrated nitric acid:—



The reaction is promoted by the presence of  $\text{H}_2\text{SO}_4$ , which serves to combine the water that is generated. The fatty bodies capable of this reaction are exceptional; the benzene derivatives, however, readily yield nitro-derivatives.

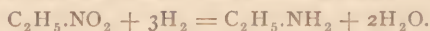


A common method for the preparation of the mono-nitro derivatives of fatty hydrocarbons — the **nitro-paraffins** — consists in heating the iodides of the alcohol radicals with silver nitrite (*V. Meyer*):—



The isomeric esters of nitrous acid, such as  $\text{C}_2\text{H}_5\text{O.NO}$  arise (see *Berichte*, 15, 1574) in this reaction. From this we would infer that silver nitrite conducted itself as if apparently consisting of  $\text{AgNO}_2$  and  $\text{AgO.NO}$ . (Potassium nitrite does not act like  $\text{AgNO}_2$ .) Since, however,  $\text{CH}_3\text{I}$  only affords nitromethane, and the higher alkyl iodides decompose more readily into alkylens the greater the quantity of nitrous acid esters, it would appear, that the formation of esters is influenced by the production of alkylens, which afterwards form esters by the union with  $\text{HNO}_2$  (compare *Annalen* 180, 157, and *Ber.* 9, 529).

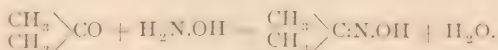
The nitro-compounds generally decompose with an explosion, if quickly heated. They are not broken up by sodium or potassium hydrate. These reagents convert the isomeric nitrous-esters, with ease, into nitrous acid and alcohol. Nascent hydrogen reduces the mono-nitro derivatives to amido-compounds, by converting the group  $\text{NO}_2$  into  $\text{NH}_2$  — the amido group:—



The compounds  $\text{C}_2\text{H}_4(\text{NO}_2)_2$ ,  $\text{C}_5\text{H}_{10}(\text{NO}_2)_2$ , etc., resulting from the action of nitrogen tetroxide upon the unsaturated hydrocarbons, must also be considered as nitro derivatives. It appears, however, that, in reality, they represent nitrous esters, since at least the so-called dinitro-amylene is not changed to an amido-compound by reducing agents. Again, some alkylens  $\text{C}_n\text{H}_{2n}$  are capable of furnishing nitro-compounds by direct nitration. (See p. 80.)

The **nitroso-compounds**, containing the group  $\text{NO}$ , attach themselves to the nitro-compounds. They sometimes arise by the action of nitrous acid — one hydrogen atom being replaced by  $\text{NO}$  (see Pseudo-nitrols, p. 82, and *Berichte*, 15, 3073). The **nitroso-amines** —  $(\text{CH}_3)_2\text{N.NO}$ , form another class of nitroso-compounds. In them the nitroso-group is bound to nitrogen.

The **isonitroso-**, or **oximido-compounds** —  $(\text{CH}_3)_2\text{C:N.OH}$  — containing the bivalent oximid group  $=\text{N.OH}$  linked to carbon — are isomeric with the above nitroso-derivatives. They are formed, especially when nitrous acid acts upon bodies containing the group  $\text{CH}_2$  attached to two  $\text{CO}$  groups. They also result from the action of hydroxylamine upon ketones  $\text{R.CO.R}$  and aldehydes  $\text{R.CO.H}$ :—



Consequently these isonitroso-compounds will be treated with the derivatives from which they originate. The so-called alkyl-nitrolic-acids may be included with them. (See p. 81.)

The nitroso derivatives (of the benzene class and the nitroso-amines) give blue colorations in their action upon a mixture of phenol and sulphuric acid, especially after dilution with water and super-saturation with alkali. The isonitroso-compounds, however, do not afford this reaction (*Berichte*, 15, 1529).

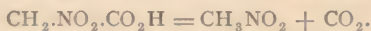
### NITRO-PARAFFINS $C_nH_{2n+1}(NO_2)$ .

Those formed by the action of silver nitrite upon the alkyl-iodides are colorless liquids almost insoluble in water. They are rather stable, distil without decomposition and decompose with difficulty. It is noteworthy that they possess an acidic character (distinctive from the halogen substitution products): this is indicated by the substitution of metals for one hydrogen atom, through the action of alkaline hydrates:—



The nitro-group always exerts such an acidic influence upon hydrogen linked to carbon; the further addition of halogens or nitro-groups increases the same, but it is confined to the hydrogen bound to the same carbon atom. Thus the compounds:  $CH_3.CHBr(NO_2)$  brom-nitroethane,  $CH_3.CH(NO_2)_2$  di-nitroethane,  $CH(NO_2)_3$  nitroform, etc., are strong acids, while  $CH_3.CBr_2(NO_2)$  and  $(CH_3)_2C(NO_2)_2$ ,  $\beta$ -dinitro propane, etc., possess neutral reaction and do not combine with bases.

**Nitromethane**,  $CH_3.NO_2$ , is produced by boiling chloracetate of potassium  $CH_2Cl.COOK$  with potassium nitrite. In this instance it is very probable nitro-acetic acid is first formed, but it subsequently breaks up into nitromethane and carbon dioxide:—



It is an agreeable-smelling, mobile liquid, sinking in water and boiling at  $101^\circ$ . Mixed with an alcoholic sodium hydrate solution it gives a crystalline precipitate  $CH_2Na(NO_2) + C_2H_6O$  which loses alcohol on standing over sulphuric acid. Salts of the heavy metals precipitate metallic compounds (like  $CH_2Ag(NO_2)$ ) from the aqueous solution. These are in most cases violently explosive. Nitromethane is liberated again from the salts by mineral acids. Heated with concentrated HCl to  $150^\circ$  nitromethane breaks up into formic acid and hydroxylamine:—



Chlorine water converts sodium nitromethane into nitrochlormethane,  $CH_2Cl(NO_2)$ , which is an oil boiling at  $122^\circ$ . In like manner, through the agency of bromine, we obtain bromnitromethane,  $CH_2Br(NO_2)$ , a pungent smelling oil, boiling at  $144^\circ$ , from which are also prepared dibrom- and tribrom-nitromethane,  $CHBr_2(NO_2)$  and  $CBr_3(NO_2)$ ,—Bromopierin (p. 84). The first three bodies react acid and dissolve in alkalis.

**Nitroethane**,  $C_2H_5.NO_2$ , is similar to nitromethane. It boils at  $113-114^\circ$  and its specific gravity at  $13^\circ$  equals 1.058. Nascent hydrogen converts it into  $C_2H_5.NH_2$ . Heated to  $140^\circ$  with concentrated hydrochloric acid, it decomposes into acetic acid and hydroxylamine. Ferric chloride imparts a blood-red color and copper sulphate a dark green to the sodium compound.

Bromine converts nitroethane in alkaline solution into bromnitroethane,  $CH_3.CHBr(NO_2)$ , an oil with a pungent odor and boiling at  $147^\circ$ , and into dibromnitroethane,  $CH_3.CBr_2.NO_2$ , boiling at  $165^\circ$ . The first reacts strongly acid and dissolves in  $NaOH$  to  $CH_3.CNaBr(NO_2)$ ; the second is neutral and insoluble in alkalis.

**$\alpha$ -Nitropropane**,  $C_3H_7.NO_2 = CH_3.CH_2.CH_2.NO_2$ , boils at  $125-127^\circ$ .

**$\beta$ -Nitropropane**— $(CH_3)_2CH.NO_2$ , boils from  $115-117^\circ$ . Both react acid and yield salts with the alkalis.

Brom- $\alpha$ -nitropropane,  $CH_3.CH_2.CHBr(NO_2)$ , boiling at  $160-165^\circ$ , has a strong acid reaction and dissolves in alkalis. On the other hand dibrom- $\alpha$ -nitropropane,  $CH_3.CH_2.CBr_2(NO_2)$ , boiling at  $185^\circ$ , is a neutral compound insoluble in alkalis. Brom- $\beta$ -nitropropane,  $(CH_3)_2CHBr(NO_2)$ , boiling at  $148-150^\circ$  is also a neutral compound (see p. 79).

**Nitrobutanes**,  $C_4H_9.NO_2$  (compare Butyl alcohols). Normal nitrobutane,  $CH_3.CH_2.CH_2.CH_2.NO_2$ , boils at  $151^\circ$  and yields normal butylamine by reduction. Secondary nitrobutane,  $CH_3.CH_2.CH(NO_2).CH_3$ ,  $\begin{matrix} C_2H_5 \\ \diagup \\ C_2H_5 \end{matrix} > CH.NO_2$ , boils about  $140^\circ$ . Nitroisobutane boils at  $137-140^\circ$  and has an odor resembling that of peppermint. The three nitrobutanes are acid, dissolve in alkalis and yield bromine derivatives. Tertiary nitrobutane,  $(CH_3)_3C.NO_2$ , on the contrary, boiling at  $120^\circ$  is a neutral compound, insoluble in alkalis.

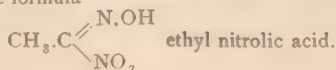
**Nitroisoamyl**,  $C_5H_{11}.NO_2$ , obtained from amyl-alcohol of fermentation, boils at  $150-160^\circ$  and yields metallic compounds.

**Nitropropylene**,  $C_3H_5.NO_2$ , allyl nitryl, from allyl bromide, is an oil boiling at  $96^\circ$ .

**Nitroalkylens**,  $C_nH_{2n-1}(NO_2)$ , are formed in the action of nitric acid upon some alkylens and tertiary alcohols. Thus there is a nitro-butylene,  $C_4H_7(NO_2)$ , obtained from isobutylene,  $(CH_3)_2C:CH_2$ , and trimethyl-carbinol  $(CH_3)_3C.OH$ . It boils about  $156^\circ$ . A nitroamylene,  $C_5H_9(NO_2)$ , is also obtained from dimethyl ethyl carbinol  $\begin{matrix} (CH_3)_2 \\ | \\ C_2H_5 \end{matrix} > C.OH$ . Upon reduction, these nitroalkylens do not yield amido-compounds, but part with the nitrogen as ammonia or hydroxylamine.

The varying deportment of the nitro-paraffins with nitrous acid (better  $NO_2K$  and  $H_2SO_4$ ) is very interesting, according as they are derived from primary, secondary or tertiary radicals. (p. 31).

On mixing the primary nitro-compounds (those in which  $NO_2$  is attached to  $CH_2$ ) with a solution of  $NO_2K$  in concentrated potassium hydrate and adding dilute  $H_2SO_4$ , the solution assumes in the beginning an *intense red* color and the so-called **Ethyl-nitrolic acids** are produced. Their structure very probably corresponds to the formula



The nitrolic acids are colorless crystalline bodies, soluble in ether. They behave like acids. Their alkali salts are dark red in color—hence the appearance, in the beginning, of a red coloration which disappears in presence of excess of sulphuric acid and reappears on addition of alkali.

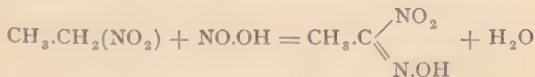
The nitro-compounds of the secondary radicals (those in which  $\text{NO}_2$  is joined to  $\text{CH}$ ), when exposed to similar treatment, yield a *dark blue* coloration and then colorless compounds—the **pseudo nitrols**—separate. These are not turned red by addition of alkali:—



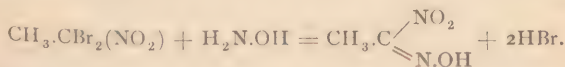
In the solid state pseudo-nitrols are colorless; when liquid or in solution they are dark blue.

The nitro-compounds of tertiary radicals (like  $(\text{CH}_3)_3\text{C}.\text{NO}_2$ ) do not react with nitrous acid and do not afford colors. Therefore the preceding reactions serve as a very delicate and characteristic means of distinguishing primary, secondary and tertiary alcoholic radicals (in their iodides) from each other (secondary nitro-pentane no longer exhibits the reaction). In a similar manner the primary and secondary nitro-derivatives may be detected in a mixture at the same time (*Berichte* 9, 539 and *Annalen* 180, 139).

The so-called alkyl-nitrolic acids, produced by the action of nitrous acid (or  $\text{NO}_2\text{K}$  and  $\text{H}_2\text{SO}_4$ ) upon the primary nitro-paraffins (see above):—



may be prepared synthetically by treating the dibrom nitro-paraffins with hydroxylamine:



Therefore they are to be regarded as isonitroso- or oximid-compounds (see p. 78).

The nitrolic acids are solid, crystalline, colorless, or faintly-yellow colored bodies, soluble in water, alcohol, ether, and chloroform. They are strong acids, and form salts with alkalies that are not very stable, yielding at the same time a dark red color. They are broken up into hydroxylamine, and the corresponding fat acids, by tin and hydrochloric acid. When heated with dilute sulphuric acid they split up into oxides of nitrogen and fatty acids.

**Methyl Nitrolic Acid**,  $\text{CH} \begin{array}{l} \nearrow \text{NO}_2 \\ \searrow \text{N.OH} \end{array}$ , forms colorless prisms, fusing at  $54^\circ$ .

It decomposes into formic acid and nitrogen oxides.



**Ethyl Nitrolic Acid**,  $\text{CH}_3.\text{C} \begin{smallmatrix} \diagup \text{NO}_2 \\ \diagdown \text{N.OH} \end{smallmatrix}$ . Bright yellow prisms, of sweet taste,

melting at  $81-82^\circ$ , and decomposing when covered with concentrated  $\text{H}_2\text{SO}_4$ , into acetic acid and nitrogen oxides.

**Propyl Nitrolic Acid**,  $\text{CH}_3.\text{CH}_2.\text{C} \begin{smallmatrix} \diagup \text{NO}_2 \\ \diagdown \text{N.OH} \end{smallmatrix}$ . Bright yellow prisms, melting

at  $60^\circ$ , with decomposition.

By the action of sodium amalgam upon the alkyl-nitrolic acids, and also upon dinitro-paraffins, we have the **Leucaurolie acids**, like  $(\text{C}_2\text{H}_4\text{N}_2\text{O})_2$ , produced. These probably correspond to the azo-compounds of the benzene group (*Annalen*, 214, 328).

The pseudo-nitrols isomeric with the nitrolic acids, and formed by the action of nitrous acid upon the secondary nitro-paraffins (see p. 81),

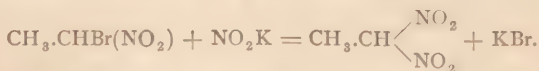


are to be viewed as nitro-nitroso compounds. They are crystalline bodies, colorless in the solid condition, but exhibiting a deep blue color when fused or dissolved (in alcohol, ether, chloroform). They react neutral, and are insoluble in water, alkalis and acids. Dissolved in glacial acetic acid, they are oxidized by chromic acid to dinitro-compounds.

**Propyl Pseudonitrol**,  $(\text{CH}_3)_2\text{C} \begin{smallmatrix} \diagup \text{NO}_2 \\ \diagdown \text{NO} \end{smallmatrix}$ , nitro-nitroso-propane, is a white powder, crystallizing from alcohol in colorless, brilliant prisms. It melts at  $76^\circ$ , to a dark blue liquid, and decomposes into oxides of nitrogen and dinitropropane. Chromic acid changes it to  $\beta$ -dinitropropane and acetone.

**Butyl Pseudonitrol**,  $\text{C}_2\text{H}_5.\text{CH} \begin{smallmatrix} \diagup \text{NO}_2 \\ \diagdown \text{NO} \end{smallmatrix}$ , is a colorless, crystalline mass, melting at  $58^\circ$ . In its fused state, or when dissolved, it exhibits a deep blue color.

The dinitro-derivatives of the paraffins are obtained by the oxidation of the pseudo-nitrols, and by action of  $\text{KNO}_2$  upon the monobrom-derivatives of the nitro-paraffins:



They also result from the acetones by action of concentrated  $\text{HNO}_3$ . Thus from diethyl ketone,  $(\text{C}_2\text{H}_5)_2\text{CO}$ , we get dinitroethane, from dipropyl ketone,  $(\text{C}_3\text{H}_7)_2\text{CO}$ ,  $\alpha$ -dinitropropane, etc. (*Berichte*, 12, 287.)

They also form in an analogous manner from the alkylized acetic acid esters (see these) on warming the latter with  $\text{HNO}_3$  (*Berichte*, 15, 1495)—



**Dinitroethane**,  $\text{CH}_3 \cdot \text{CH}(\text{NO}_2)_2$ , from brom-nitroethane, is a colorless oil, of specific gravity 1.35 at  $23^\circ$ . It boils at  $185\text{--}186^\circ$ . Tin and hydrochloric acid change it to hydroxylamine, aldehyde and acetic acid. It reacts acid and dissolves in potassium hydrate, forming  $\text{CH}_3 \cdot \text{CK}(\text{NO}_2)_2$ , which crystallizes in yellow prisms. An oil,  $\text{CH}_3 \cdot \text{CBr}(\text{NO}_2)_2$ , that cannot be distilled is produced by the action of bromine.

**$\alpha$ -Dinitropropane**,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{NO}_2)_2$ , from brom-nitropropane, is a colorless oil of specific gravity 1.258 at  $22^\circ$ ; it boils at  $189^\circ$ , reacts acid and dissolves in the alkalis, forming salts.

**$\beta$ -Dinitropropane**,  $(\text{CH}_3)_2\text{C}(\text{NO}_2)_2$ , is also produced by acting upon isobutyric and isovaleric acids (*Berichte*, 15, 2325) with  $\text{HNO}_3$ . It forms white camphor-like crystals, fusing at  $53^\circ$  and boiling at  $185.5^\circ$ . It is neutral and insoluble in alkalis. Tin and hydrochloric acid change it to acetone and hydroxylamine.

**$\beta$ -Dinitrobutane**,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{C}(\text{NO}_2)_2 \cdot \text{CH}_3$ , from butyl pseudo-nitrol, boils at  $199^\circ$  and does not dissolve in alkalis. Hydroxylamine and methyl ethyl ketone are the products it furnishes when acted upon by tin and hydrochloric acid.

We may note the following among the nitro-compounds, resulting from the action of nitric acid:—

**Nitroform**,  $\text{CH}(\text{NO}_2)_3$ , Trinitromethane, is produced in slight quantity when nitric acid acts upon various carbon compounds. It is most conveniently prepared from trinitro-acetonitrile  $\text{C}_2(\text{NO}_2)_3\text{N}$ . (See this.) When the latter is boiled with water, carbon dioxide is generated, and the ammonium salt of nitroform produced:—



Trinitro-Acetonitrile

Ammonium Nitroform.

The last is a yellow crystalline compound, from which concentrated sulphuric acid separates free nitroform. This is a colorless, thick oil, solidifying below  $+15^\circ$  to a solid, consisting of cubes. It dissolves rather easily in water, imparting to the latter a yellow color. It explodes when heated rapidly.

Nitroform behaves like a strong acid; the presence of three nitro-groups imparts to hydrogen, in union with carbon, an acid character. Therefore it unites with  $\text{NH}_3$  and the alkalis to form salts like  $\text{C}(\text{NO}_2)_3\text{K}$ , from which acids again liberate nitroform (p. 79). The hydrogen of nitroform can also be replaced by bromine or  $\text{NO}_2$ .

**Brom-nitroform**,  $\text{C}(\text{NO}_2)_3\text{Br}$ , Brom-trinitromethane, is produced by permitting bromine to act for several days upon nitroform exposed to sunlight. The reaction takes place more rapidly by adding bromine to the aqueous solution of the mercury salt of nitroform. In the cold it solidifies to a white crystalline mass, fusing at  $+12^\circ$ . It volatilizes in steam without decomposition.

**Tetranitromethane**,  $C(NO_2)_4$ , results on heating nitroform with a mixture of fuming nitric acid and sulphuric acid. It is a colorless oil that solidifies to a crystalline mass, fusing at  $13^\circ$ . It is insoluble in water, but dissolves readily in alcohol and ether. It is very stable, and does not explode on application of heat, but distils at  $126^\circ$  without sustaining any decomposition.

**Nitrochloroform**,  $C(NO_2)Cl_3$ —Chloropicrin, trichlor-nitromethane, is frequently produced in the action of nitric acid upon chlorinated carbon compounds (chloral), and also when chlorine or bleaching powder acts upon nitro-derivatives (fulminating mercury, picric acid and nitromethane).

In the preparation of chloropicrin, 10 parts of freshly prepared bleaching powder are mixed to a thick paste with cold water and placed in a retort. To this is added a saturated solution of picric acid, heated to  $30^\circ$ . Usually the reaction occurs without any additional heat, and the chloropicrin distils over with the aqueous vapor (*Annalen*, 139, 111).

Chloropicrin is a colorless liquid, boiling at  $112^\circ$ , and having a specific gravity of 1.692 at  $0^\circ$ . It possesses a very penetrating odor that attacks the eyes powerfully. It explodes when rapidly heated. When treated with acetic acid and iron filings it is converted into methylamine :



**Bromopicrin**,  $CBr_3(NO_2)$ —Tribrom-nitromethane, is formed, like the preceding chloro-compound, by heating picric acid with calcium hypobromite (calcium hydroxide and bromine), or by heating nitromethane with bromine (p. 79). It closely resembles chloropicrin and yields crystals below  $+10^\circ$ . It can be distilled in a vacuum without decomposition.

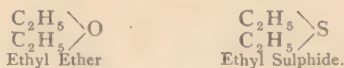
## ALCOHOLS, ACIDS AND THEIR DERIVATIVES.

All organic compounds are derived from the hydrocarbons, the simplest derivatives of carbon, by the replacement of the hydrogen atoms by other atoms or atomic groups. The different groups of chemical bodies are characterized in their specific properties by the presence of such substituting side-groups. Thus the alcohols contain OH, the aldehydes CHO, the acids COOH, etc., etc.

In the following pages we will consider the carbon compounds according to the number of side groups yet capable of replacement—as monovalent, divalent, trivalent, etc., compounds. To each of these groups other derivatives are attached bearing intimate genetic connection with them.

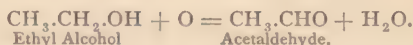
By the replacement of one atom of hydrogen of hydrocarbons by the hydroxyl group OH we get the **monovalent** (monohydric) **alcohols**, e. g.  $C_2H_5.OH$ , in which the H of OH is capable

of further exchange. The thio-alcohols or mercaptans, *e. g.* ethyl mercaptan,  $C_2H_5SH$ , are analogous to these. **Ethers** result from the union of two monovalent alcohol radicals through the agency of an oxygen atom; corresponding to these are the thio-ethers or sulphur alkyls :

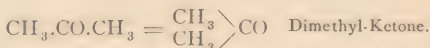


The **Amines**,  $C_2H_5NH_2$ , **Phosphines** and the so-called **metallo-organic compounds** are also derivatives of the alcohol radicals.

When two hydrogen atoms of a methyl group,  $CH_3$ , of the hydrocarbons are replaced by one oxygen atom the **aldehydes** result. These are easily obtained from the alcohols by oxidation :

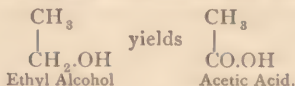


The group  $CHO$  (aldehyde group) is characteristic of aldehydes. The **ketones** are compounds in which two hydrogen atoms of an intermediate carbon atom (see p. 25) are replaced by one atom of oxygen :

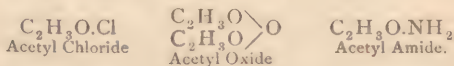


They are characterized by the group  $CO$ , united to two alkyls.

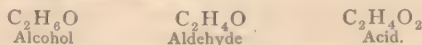
When the two hydrogen atoms attached to the carbon carrying  $OH$  are replaced by oxygen, we obtain the **monobasic acids** :



The **carboxyl** group— $CO \cdot OH$ —is characteristic of organic acids. The hydrogen atom present in it may be readily replaced by metals, giving rise to salts. Or, the acids may be viewed as compounds of  $OH$  with residual atomic groups (*e. g.*  $CH_3 \cdot CO = C_2H_3O$ , acetyl) designated **acid radicals**. The latter, like the alcoholic radicals, are capable of entering into further combinations :



The following formulas exhibit the connection between alcohols, aldehydes (or ketones) and acids :



The unsaturated hydrocarbons also yield *unsaturated* alcohols, aldehydes, acids, etc.



The dihydric alcohols, known as *glycols*, are formed when two hydrogen atoms of the hydrocarbons are replaced by hydroxyl:



In these four hydrogen atoms can be replaced by oxygen, giving rise to the dihydric *monobasic* and the dihydric *dibasic* acids.



The number of CO.OH groups in the acids determines their basicity. The number of hydroxyl groups present is indicated by the terms *mono-valent*, *di-valent*, etc. In the same manner, tri-valent (trihydric), mono-, di- and tri-basic acids, etc., are derived from the trivalent alcohols.

The relations of the alcohols and acids to each other, with reference to their valence and basicity, is manifest from the following table:—

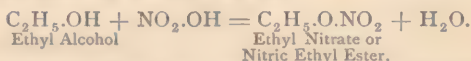
	ALCOHOLS.	ACIDS.		
		1-basic.	2-basic.	3-basic.
Monovalent.	$\text{CH}_3\cdot\text{OH}$ Methyl Alcohol.	$\text{CHO}\cdot\text{OH}$ Formic Acid.		
	$\text{C}_2\text{H}_5\cdot\text{OH}$ Ethyl Alcohol.	$\text{CH}_3\cdot\text{COOH}$ Acetic Acid.		
Divalent.	$\begin{array}{c} \text{CH}_2\cdot\text{OH} \\   \\ \text{CH}_2\cdot\text{OH} \end{array}$ Ethylene Glycol.	$\begin{array}{c} \text{CH}_2\cdot\text{OH} \\   \\ \text{CO}\cdot\text{OH} \end{array}$ Glycollic Acid.	$\begin{array}{c} \text{CO}\cdot\text{OH} \\   \\ \text{CO}\cdot\text{OH} \end{array}$ Oxalic Acid.	
	$\text{C}_3\text{H}_6(\text{OH})_2$ Propylene Glycol.	$\text{C}_2\text{H}_4 \begin{array}{l} \text{OH} \\ \text{CO}\cdot\text{OH} \end{array}$ Lactic Acid.	$\text{CH}_2 \begin{array}{l} \text{CO}\cdot\text{OH} \\ \text{CO}\cdot\text{OH} \end{array}$ Malonic Acid.	
Trivalent.	$\begin{array}{c} \text{CH}_2\cdot\text{OH} \\   \\ \text{CH}\cdot\text{OH} \\   \\ \text{CH}_2\cdot\text{OH} \end{array}$ Glycerine.	$\begin{array}{c} \text{CH}_2\cdot\text{OH} \\   \\ \text{CH}\cdot\text{OH} \\   \\ \text{CO}\cdot\text{OH} \end{array}$ Glyceric Acid.	$\begin{array}{c} \text{CO}\cdot\text{OH} \\   \\ \text{CH}\cdot\text{OH} \\   \\ \text{CO}\cdot\text{OH} \end{array}$ Oxymalonic Acid.	$\text{C}_3\text{H}_5 \begin{cases} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{cases}$ Tricarballic Acid.
Tetra-valent.	$\text{C}_4\text{H}_6(\text{OH})_4$ Erythrite.	$\text{C}_4\text{H}_4\text{O}_2(\text{OH})_4$ Erythric Acid.	$\text{C}_4\text{H}_2\text{O}_2(\text{OH})_4$ Tartaric Acid.	$\text{C}_6\text{H}_4\text{O}_3(\text{OH})_4$ Citric Acid.
Hexa-valent.	$\text{C}_6\text{H}_8(\text{OH})_6$ Mannite.	$\text{C}_6\text{H}_6\text{O}_2(\text{OH})_6$ Mannitic Acid.	$\text{C}_6\text{H}_4\text{O}_2(\text{OH})_6$ Mucic Acid.	

# MONOVALENT COMPOUNDS.

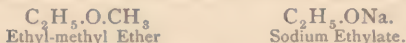
## MONOVALENT ALCOHOLS.

### MONOHYDRIC ALCOHOLS.

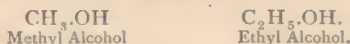
The monovalent alcohols contain one hydroxyl group, OH; bivalent oxygen links the monovalent alcohol radical to hydrogen:  $\text{CH}_3\text{O.H}$ , methyl alcohol. This hydrogen atom is characterized by its ability, in the action of acids upon alcohol, to exchange itself for acid residues, forming compound ethers or *esters*, corresponding to the salts of mineral acids:



Alkyls and metals can also replace the hydrogen in alcohol—



**Structure of the Monovalent Alcohols.** The possible isomeric alcohols may be readily derived from the hydrocarbons; they correspond to the mono-halogen isomerides (p. 29). There is only one possible structure for the first two members of the normal alcohols:—



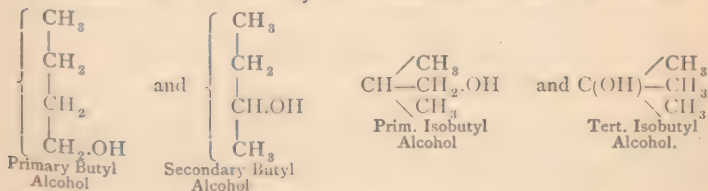
Two isomerides can be obtained from propane,  $\text{C}_3\text{H}_8 = \text{CH}_3.\text{CH}_2.\text{CH}_3$ :—



Two isomerides correspond to the formula  $\text{C}_4\text{H}_{10}$  (p. 49)—



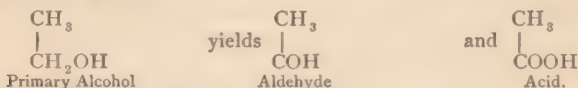
Two isomeric alcohols may be obtained from each of these:—



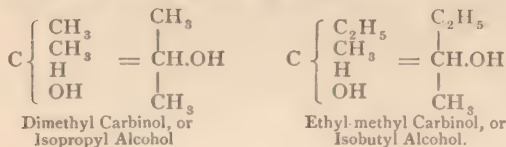
The following is a very good method of formulating the alcohols. They are considered as derivatives of methyl alcohol or *carbinol*,  $\text{CH}_3.\text{OH}$ . By the replacement of one hydrogen atom in carbinol by alkyls (p. 31) the *primary alcohols* result:—



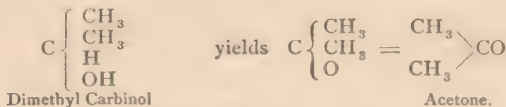
If the replacing group possesses normal structure, the primary alcohols are said to be *normal*. In alcohols of this class the carbon atom carrying the hydroxyl group has two additional hydrogen atoms. Hence compounds of this variety may very easily pass into aldehydes (with group COH) and acids (with COOH group) on oxidation (see p. 85):—



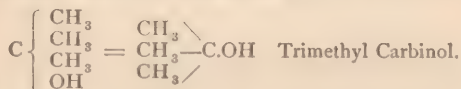
The *secondary alcohols* result when two hydrogen atoms in carbinol,  $\text{CH}_3\text{.OH}$ , are replaced by alkyls:—



In alcohols of this class the carbon atom carrying the OH group has but one additional hydrogen atom. They do not furnish corresponding aldehydes and acids. When oxidized they pass into ketones (p. 85):—

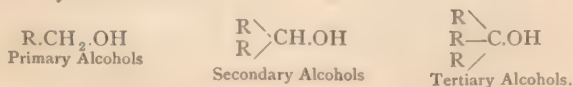


When, finally, all three hydrogen atoms in carbinol are replaced by alkyls, we get the *tertiary alcohols*:—



These are not capable of forming corresponding aldehydes, acids or ketones. Under the influence of strong oxidizing agents they suffer a decomposition; and acids having a less number of carbon atoms result.

Primary alcohols, therefore, contain the group  $\text{CH}_2\text{.OH}$  joined to *one* alcohol radical (in methyl alcohol it is linked to H); the group  $\text{CH.OH}$  linked to two alkyls is peculiar to secondary alcohols; while in tertiary alcohols the C in combination with OH has three alkyls attached to it:—



The secondary and tertiary alcohols, in distinction from the primary or true alcohols, are designated **pseudo-alcohols**. They have the power of forming esters (p. 87).

*Formation of Alcohols.*—The most important methods of preparing the monohydric alcohols are the following:—

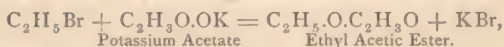
(1) The replacement of the halogen of monosubstituted hydrocarbons by hydroxyl. This is most easily effected by the action of freshly precipitated, moist silver oxide. It acts in this instance like an hydroxide:—



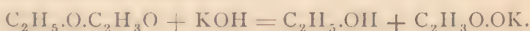
In many cases the change is best brought about by heating the halogen derivatives with lead oxide and water; the formation of alkylens is avoided in this way. The iodides are more reactive than the chlorides or bromides. Even heating with water alone at high temperatures causes a partial transposition of halogen into hydroxyl derivatives. The halogen derivatives of the secondary and tertiary radicals are very reactive. If heated for some time with 10–15 volumes  $\text{H}_2\text{O}$  to  $100^\circ$  they are completely converted into alcohols (*Annalen*, 186, 390).

Water at ordinary temperatures converts the tertiary alkyl iodides into alcohols. Heated to  $100^\circ$  with methyl alcohol they pass into alcohols and methyl iodide (*Annalen*, 220, 158).

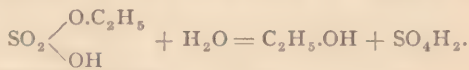
It is often more practical to first convert the halogen derivatives into acetic acid esters, by heating with silver or potassium acetate:—



and then boil these with potassium or sodium hydrate (saponification), and obtain the alcohols:—

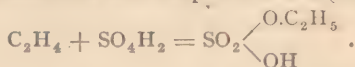


(2) By decomposing the acid esters of sulphuric acid with boiling water:—

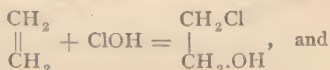


Ethyl Sulphuric Acid.

These esters may be easily obtained by directly combining the unsaturated hydrocarbons with sulphuric acid (see p. 55):



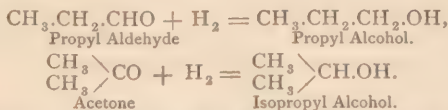
A like conversion of unsaturated hydrocarbons is attained by means of hypochlorous acid; the chlorine derivatives first produced are further changed by nascent hydrogen:





Many alkylens (like iso- and pseudo butylene) dissolve at once in dilute nitric acid, absorb water, and yield alcohols (*Annalen*, 180, 245.)

(3) By acting on the aldehydes and ketones with nascent hydrogen. The former yield primary, and the latter secondary, alcohols (compare p. 88):—



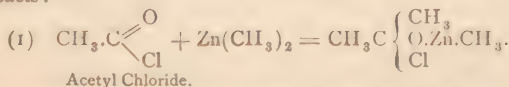
Sodium amalgam in presence of dilute sulphuric or acetic acid will effect this reduction. It is, however, best to use iron filings and 50 per cent. acetic acid (Lieben), or zinc dust and glacial acetic acid, when the acetic esters will be formed at first (*Berichte*, 16, 1715).

(4) A very remarkable synthetic method, which led to the discovery of the **tertiary** alcohols, consists, in the action of the zinc compounds of the alkyls upon the chlorides of the acid radicals. The product is then further changed by the action of water (Butlerow). Thus, from acetyl chloride and zinc methyl, we obtain trimethyl carbinol ( $\text{CH}_3)_3\text{C.OH}$ :—

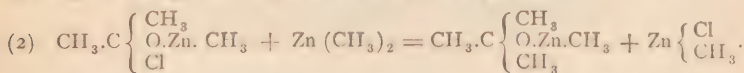


The acid chloride (1 molecule) is added, drop by drop, to zinc methyl (2 molecules), cooled with ice, and allowed to remain undisturbed for some hours in the cold, until the mass has become crystalline. After subsequent exposure for two or three days, at ordinary temperatures, the product is decomposed with ice water. Ketones are formed if water be added any sooner (*Annalen*, 188, 121 u. 113.)

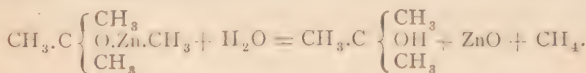
The reaction divides itself into three phases. At first only one molecule of zinc alkyl reacts:—



The resulting compound gives a crystalline product with the second molecule of the zinc alkyl, and this immediately decomposed with water yields acetone. By longer standing, however, further reaction takes place:—



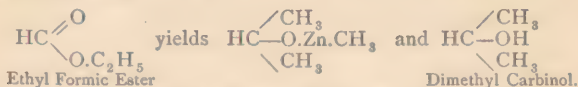
If now water be permitted to take part, a tertiary alcohol will be formed from the first body. The equation is:



If in the second stage the zinc compound of another radical be employed, the latter may be introduced, and in this manner we obtain tertiary alcohols with two or three different alkyls (*Annalen*, 175, 261, and 188, 110, 122).

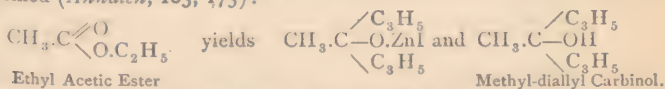
It is remarkable that only zinc methyl and ethyl furnish tertiary alcohols, while zinc propyl affords only those of the secondary type. (*Berichte*, 16, 2284.)

(5) Just as we obtained tertiary alcohols from the acid radicals, so can we derive secondary alcohols from the acetic acid esters. Zinc alkyls are allowed to react in this case (or alkyl iodides and zinc), and two alkyls are introduced. At first crystalline intermediate products are produced; these yield the alcohols when treated with water:

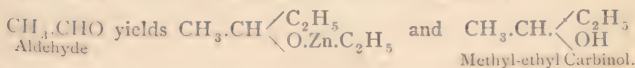


Using some other zinc alkyl in the second stage of the reaction, or by working with a mixture of two alkyl iodides and zinc, two different alkyls may also be introduced here (*Annalen*, 175, 362, 374).

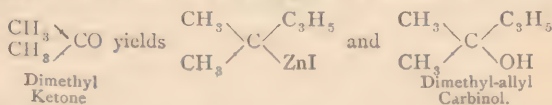
Zinc and an alkyl iodide (not ethyl-iodide, however) react similarly upon acetic acid esters. Two alkyl groups are introduced and unsaturated tertiary alcohols formed (*Annalen*, 185, 175):



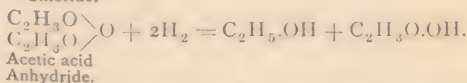
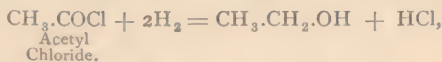
When zinc alkyls act upon aldehydes, only one alkyl group enters, and the reaction product of the first stage yields a secondary alcohol when treated with water. (Compare *Annalen*, 213, 369, and *Berichte*, 14, 2557):



We get unsaturated tertiary alcohols from the ketones by the action of zinc and allyl iodide (not ethyl iodide). An allyl group is introduced:

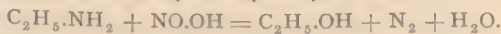


(6) By the action of nascent hydrogen upon the chlorides of acid radicals or acid anhydrides:



Very probably aldehydes are produced at the beginning and are subsequently reduced to alcohols (see p. 95). Only primary alcohols result by this reaction. Sodium amalgam, or better sodium, serves as the reducing agent. (*Berichte*, 9, 1312.)

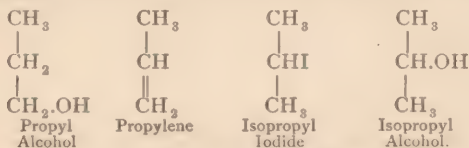
(7) Action of nitrous acid upon the primary amines:



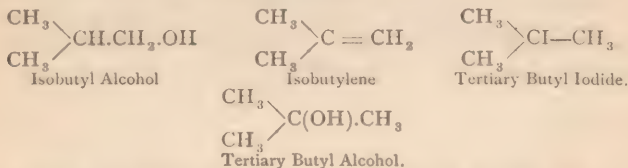
Very often transpositions occur with the higher alkyl-amines and instead of the primary we obtain secondary alcohols. (Compare *Berichte*, 16, 744.)

In addition to the above universal methods, alcohols are formed by various other reactions. Their formation in the alcoholic fermentation of sugars in the presence of ferments is of great practical importance. Appreciable quantities of methyl alcohol are produced in the dry distillation of wood. Many alcohols, too, exist, as already formed natural products in compounds, chiefly as compound ethers of organic acids.

*Conversion of Primary into Secondary and Tertiary Alcohols.* By the elimination of water the primary alcohols become unsaturated hydrocarbons  $C_n H_{2n}$  (p. 54). The latter, treated with concentrated  $H_2SO_4$ , yield iodides of secondary alcoholic radicals, as iodine does not attach itself to the terminal but to the less hydrogenized carbon atom (p. 64). Secondary alcohols appear when these iodides are acted upon with silver oxide. The successive conversion is illustrated in the following formulas:—

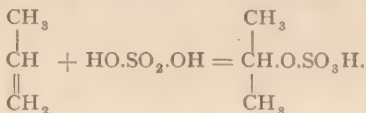


Primary alcohols in which the group  $CH_2.OH$  is joined to a secondary radical, pass in the same manner into tertiary alcohols—



The change is more satisfactorily effected by the aid of sulphuric acid.

The sulphuric esters (p. 55) arising from the alkylens have the sulphuric acid residue linked to the carbon atom, with the least number of attached hydrogen atoms—



When these are boiled with water they pass into alcohols.

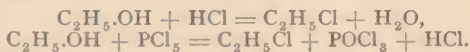
*Properties and Transpositions.* The alcohols are neutral, being neither acid nor basic compounds. They resemble the bases, in that by their action with acids they yield esters (compound ethers), which correspond to salts. In this change, the hydrogen atom of the OH group is replaced by an acid radical (p. 87). Na and K can also replace this hydrogen atom, and then we obtain the so-called metallic alcoholates.

In physical properties alcohols exhibit a gradation corresponding to their increase in molecular weight. This is true of other bodies belonging to homologous series. The lower alcohols are mobile liquids, dissolving readily in water, and possessing characteristic odor; the intermediate members are more oily, and are difficultly soluble in water, while the higher are crystalline solids, without odor or taste. They resemble the fats. Their boiling points increase gradually (with similar structure) in proportion to the increase of their molecular weights. This is about  $19^\circ$  for the difference,  $\text{CH}_2$ . The primary alcohols boil higher (about  $5^\circ$ ) than the isomeric secondary, and the latter higher than the tertiary. Here we observe again that the boiling points are lowered with the accumulation of methyl groups (see p. 48). The higher members are not volatile without decomposition. By distillation they partially break up into water and hydrocarbons  $\text{C}_n\text{H}_{2n}$  (p. 54).

Oxidizing agents ( $\text{K}_2\text{CrO}_4$  and  $\text{H}_2\text{SO}_4$ ) convert the primary alcohols first into aldehydes and then into acids; those of secondary form yield ketones, and the tertiary suffer a partial decomposition (p. 88). The three varieties of alcohols may be readily distinguished by converting them into their iodides and then into the nitro-derivatives, which afford characteristic color reactions (p. 80).

Primary and secondary alcohols, heated with acetic acid, yield esters of the latter; the tertiary, on the contrary, lose water and pass into alkylens (*Annalen*, **220**, 165).

When the alcohols are heated with the hydrogen haloids, or what is better, with the halogen derivatives of phosphorus, they are transformed into their corresponding halogen compounds (see p. 65):—



These derivatives are therefore designated also *halogen esters* of the alcohols.

Hydrogen (nascent) acting on these, causes a change back into the corresponding hydrocarbons.

Other changes of alcohols will be noted later.

#### (1) THE ALCOHOLS, $\text{C}_n\text{H}_{2n+1}\cdot\text{OH}$ .

Methyl Alcohol,	$\text{CH}_3\text{O}$	$= \text{CH}_3\cdot\text{OH}$
Ethyl “	$\text{C}_2\text{H}_5\text{O}$	$= \text{C}_2\text{H}_5\cdot\text{OH}$
Propyl Alcohols,	$\text{C}_3\text{H}_7\text{O}$	$= \text{C}_3\text{H}_7\cdot\text{OH}$
Butyl “	$\text{C}_4\text{H}_{10}\text{O}$	$= \text{C}_4\text{H}_9\cdot\text{OH}$
Amyl “	$\text{C}_5\text{H}_{12}\text{O}$	$= \text{C}_5\text{H}_{11}\cdot\text{OH}$
Hexyl “	$\text{C}_6\text{H}_{14}\text{O}$	$= \text{C}_6\text{H}_{13}\cdot\text{OH}$
Heptyl “	$\text{C}_7\text{H}_{16}\text{O}$	$= \text{C}_7\text{H}_{15}\cdot\text{OH}$ , etc.
Cetyl Alcohol,	$\text{C}_{16}\text{H}_{34}\text{O}$	$= \text{C}_{16}\text{H}_{33}\cdot\text{OH}$
Ceryl “	$\text{C}_{27}\text{H}_{56}\text{O}$	$= \text{C}_{27}\text{H}_{55}\cdot\text{OH}$
Melissyl “	$\text{C}_{30}\text{H}_{62}\text{O}$	$= \text{C}_{30}\text{H}_{61}\cdot\text{OH}$ .



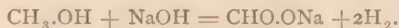
1. **Methyl Alcohol**,  $\text{CH}_3\text{OH}$ , wood spirit, occurs among the dry distillation products of wood. We find the methyl group in various natural products, and from them it may be eliminated in the form of the above alcohol. Thus from wintergreen oil, the methyl ester of salicylic acid, methyl alcohol is obtained by boiling with potassium hydroxide.

Methyl alcohol is a mobile liquid, with spirituous odor, boiling at  $66^\circ$  (the apparent boiling point can vary very much, according to the nature of the vessel), and having a sp. gr. of 0.796 at  $20^\circ$ . It mixes with water, alcohol, and ether. Its aqueous mixtures have a sp. gr. almost like that of mixtures of ethyl alcohol and equal amounts of water.

The aqueous product obtained in the distillation of wood contains methyl alcohol, acetone, acetic acid, methyl acetic ester, and other compounds, and is distilled over burnt lime. The resulting crude wood spirit contains, yet, chiefly acetone. To further purify it, anhydrous calcium chloride is added, and with this it unites to a crystalline compound. The latter is separated, freed from acetone by distillation, and afterward decomposed by distilling with water. Pure aqueous methyl alcohol passes over; this is dehydrated with lime. To procure it perfectly pure, it is only necessary to break up oxalic methyl ester, or methyl acetic ester, with KOH.

To detect ethyl in methyl alcohol, heat the latter with concentrated  $\text{H}_2\text{SO}_4$ , when acetylene will be formed from the first. Under this treatment, methyl alcohol becomes methyl ether. The amount of methyl alcohol in wood spirit is determined, quantitatively, by converting it into methyl iodide,  $\text{CH}_3\text{I}$ , through the agency of  $\text{PI}_3$  (*Berichte*, 9, 1928). We estimate the quantity of acetone by the iodoform reaction (*Berichte*, 73, 1000).

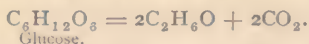
Wood spirit is employed as a source of heat, and as a solvent for gums and resins. It combines directly with  $\text{CaCl}_2$ , to form  $\text{CaCl}_2 \cdot 4\text{CH}_3\text{O}$ , crystallizing in brilliant six-sided plates. The alcohol in this salt conducts itself like water of crystallization. Potassium and sodium dissolve in anhydrous alcohol, to form methylates, *e.g.*,  $\text{CH}_3\text{ONa}$  (see potassium ethylate, p. 96). Barium oxide dissolves in it to yield a crystalline compound ( $\text{BaO} \cdot 2\text{CH}_3\text{O}$ ). When methyl alcohol is heated with soda-lime, sodium formate results:—



Oxidizing agents and also air, in presence of platinum black, change methyl alcohol to formic aldehyde and formic acid.

2. **Ethyl Alcohol**,  $\text{C}_2\text{H}_5\text{OH}$ , may be obtained from ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}$ , and from ethylene,  $\text{C}_2\text{H}_4$ , according to the general methods previously described (p. 89). Its formation in the spirituous fermentation of different varieties of sugar, *e.g.*, grape sugar, invert sugar, maltose—is practically very important. It is induced by yeast cells, occurs only in dilute aqueous solution at temperatures ranging from  $5$ – $30^\circ$ , and demands the presence of mineral salts (especially phosphates) and nitrogenous substances

(compare Fermentation). Alcoholic fermentation may set in under certain conditions, in ripe fruits, even in the absence of yeast. The various sugars when fermenting break up principally into ethyl alcohol and carbon dioxide:—



Other compounds, like propyl, butyl and amyl alcohols (the fusel alcohols), glycerol, and succinic acid, are produced in small quantities at the same time.

The crude spirit obtained from the fermented aqueous solution (of the fermented mash) by distillation is further purified on an extensive scale by fractional distillation in a column apparatus (p. 38). The first portion of the distillate contains the more volatile bodies, like aldehyde, acetal and other substances. Next comes a purer spirit, containing 90-96 per cent. alcohol, and after this common spirit, containing the fusel oils. To remove the latter entirely, the spirit, before distillation and after dilution with water, is filtered through ignited wood charcoal, which retains the fusel oils.

To prepare anhydrous alcohol, the rectified spirit (90-95 per cent. alcohol) is distilled with substances having greater attraction for water than alcohol itself. For this purpose calcium chloride, ignited potashes, or, better, caustic lime (*Annalen*, 160, 249), or barium oxide may be employed. Absolute alcohol dissolves barium oxide, assuming a yellow color at the same time. It is soluble without turbidity in a little benzene; when more than three per cent. water is present cloudiness ensues. On adding anhydrous or absolute alcohol to a mixture of very little anthraquinone and some sodium amalgam it becomes dark green in color, but in the presence of traces of water a red coloration appears (*Berichte*, 10, 927). Traces of alcohol in solutions are detected and determined either by oxidation to aldehyde (see this) or by converting it by means of dilute potash and some iodine into iodoform (*Berichte*, 13, 1002).

Absolutely pure alcohol possesses an agreeable ethereal odor, boils at  $78.3^\circ$ , and has a specific gravity of 0.80625 at  $0^\circ$ , or 0.78945 at  $20^\circ$ . At  $-90^\circ$  it is a thick liquid, at  $-130^\circ$  it solidifies to a white mass. It absorbs water energetically from the air. When mixed with water a contraction occurs, accompanied by rise of temperature; the maximum is reached when one molecule of alcohol is mixed with three molecules of water, corresponding to the formula,  $\text{C}_2\text{H}_5\text{O} + 3\text{H}_2\text{O}$ . The amount of alcohol in aqueous solutions is given either in per cents. by weight (degrees according to Richter) or volume per cents. (degrees according to Tralles).

Alcohol dissolves many mineral salts, the alkalies, hydrocarbons, resins, fatty acids, and almost all the carbon derivatives. The most of the gases are more readily soluble in it than in water; 100 volumes of alcohol dissolve 7 volumes of hydrogen, 25 volumes of oxygen, and 13 volumes of nitrogen.

Ethyl alcohol forms crystalline compounds with some salts, like calcium chloride and magnesium chloride. It plays the rôle of water of crystallization in them.

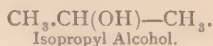
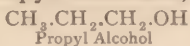
Potassium and sodium dissolve in it (also in all other alcohols)

separating hydrogen from the hydroxyl group and yielding the so-called metal alcoholates, *e. g.*,  $C_2H_5.ONa$ . All the alcohol cannot be thus changed; on evaporating the excess, white crystalline compounds  $C_2H_5.ONa$  or  $C_2H_5.OK$ , having two and three molecules of alcohol, remain. The pure ethylates are white voluminous powders, after heating to  $200^\circ$ . Excess of water converts them into alcohol and sodium hydroxide. When but little water is employed the transposition is only partial. Hence the ethylates are also formed in dissolving  $KOH$  and  $NaOH$  in strong alcohol. Other metallic oxides, *e. g.*, barium oxide, afford similar derivatives. When aluminium and iodine act upon ethyl and other alcohols, aluminium alcoholates *e. g.*, aluminium ethylate,  $Al(OC_2H_5)_3$ , result; these can be distilled in *vacuo*.

Oxidizing agents ( $MnO_2$  and  $H_2SO_4$ , chromic acid, platinum black and air) convert ethyl alcohol into acetaldehyde and acetic acid. Nitric acid changes it at  $20-30^\circ$  into glyoxal, glyoxylic acid, glycollic acid and oxalic acid. When acted upon by chlorine and bromine, chloral and bromal ( $CCl_3.CHO$  and  $CBr_3.CHO$ ) are produced.

**Trichlor-Ethyl Alcohol**,  $CCl_3.CH_2.OH$ , resulting from the action of zinc ethyl upon chloral, consists of white rhombic crystals, fusing at  $17.8^\circ$  and boiling at  $151^\circ$ ; specific gravity 1.55 at  $23^\circ$ . It is slightly soluble in water, but readily soluble in alcohol and ether. When oxidized with nitric acid, it yields trichloroacetic acid (*Annalen*, 210, 83).

### 3. Propyl Alcohols, $C_3H_7.OH$ :—



(1) **Normal Propyl Alcohol**,  $CH_3.CH_2.CH_2.OH$ , is produced in the fermentation of sugars, etc. It may be obtained from fusel oil by distillation (p. 95). To get it perfectly pure, the corresponding bromide is converted into the acetate, and this broken up by potassium hydrate. It may be artificially prepared from propyl aldehyde and propionic anhydride by the action of nascent hydrogen (sodium amalgam). It is an agreeable-smelling liquid of specific gravity 0.8044 at  $20^\circ$ , and boiling at  $97.4^\circ$ . The boiling point is very materially affected by slight additions of water, as a hydrate,  $C_3H_8O + H_2O$ , is formed, which boils at  $87^\circ$ . It is miscible in every proportion with water, but on the addition of calcium chloride and other easily soluble salts, it separates again from its aqueous solution. Hence it is insoluble in a saturated, cold calcium chloride solution, and this distinguishes it from ethyl alcohol.

It passes into propionic aldehyde and propionic acid, under the influence of oxidizing agents. When heated with 5 volumes of  $H_2SO_4$ , it yields propylene. Its chloride boils at  $46.5^\circ$ , the bromide at  $71^\circ$ , the iodide at  $102^\circ$  (p. 68).

(2) **Secondary or Isopropyl Alcohol**,  $(\text{CH}_3)_2\text{CH.OH}$ , dimethyl carbinol, is prepared from the iso-iodide (p. 68); from acetone by the action of sodium amalgam; from acrolein,  $\text{C}_3\text{H}_4\text{O}$ , propylene oxide,  $\text{C}_3\text{H}_6\text{O}$ , and dichlorhydrin,  $\text{C}_2\text{H}_5\text{Cl}_2.\text{OH}$ , by means of nascent hydrogen; from glycol iodhydrin,  $\text{C}_2\text{H}_4\text{I.OH}$ , by action of zinc methyl; from propylamine (p. 91) by action of nitrous acid, and from formic ester by the aid of zinc and methyl iodide (p. 91).

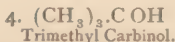
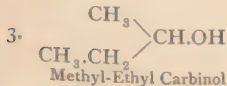
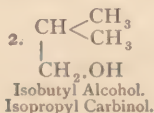
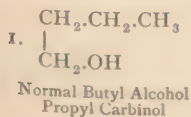
To prepare isopropyl alcohol, a mixture of one volume acetone and five volumes of water is shaken with liquid sodium amalgam, and the distillate repeatedly subjected to the same treatment, until an energetic liberation of hydrogen is perceptible. It is then distilled and the distillate dehydrated with ignited potashes and afterwards mixed with pulverized calcium chloride. The resulting crystalline compound is deprived of all adhering acetone by standing over sulphuric acid. If heated, it breaks up into  $\text{CaCl}_2$  and isopropyl alcohol.

The most practical method of obtaining it is to boil the iodide with ten parts of water and freshly prepared lead hydroxide in a vessel connected with a return condenser, or simply by heating the iodide with twenty volumes of water to  $100^\circ$  (*Annalen*, 186, 391).

Isopropyl alcohol boils at  $82.8^\circ$ , and has a specific gravity 0.7887 at  $20^\circ$ . It is miscible with water, alcohol and ether; potash will separate it again from the aqueous solution. Oxidizing agents convert it into acetone. Its chloride,  $\text{C}_3\text{H}_7\text{Cl}$ , boils at  $37^\circ$ , the bromide at  $60-63^\circ$ , and the iodide at  $89^\circ$  (p. 69). The benzoic ester,  $\text{C}_3\text{H}_7\text{O.C}_7\text{H}_5\text{O}$ , breaks up on distillation into benzoic acid and propylene.

**Trichlorisopropyl Alcohol**,  $\begin{array}{c} \text{CCl}_3 \\ \text{CH}_3 \end{array} \text{CH.OH}$ , is produced in the action of zinc methyl on chloral. It is crystalline, fuses at  $49^\circ$ , and boils about  $155^\circ$  (*Annalen*, 210, 78).

4. **Butyl Alcohols**,  $\text{C}_4\text{H}_9.\text{OH}$ . According to theory four isomerides are possible: 2 primary, 1 secondary, and 1 tertiary (p. 87):—



(1) **Normal Butyl Alcohol**,  $\text{C}_3\text{H}_7.\text{CH}_2.\text{OH}$ , forms in the action of sodium amalgam upon normal butyl aldehyde,  $\text{C}_3\text{H}_7.\text{COH}$ , upon butyryl chloride,  $\text{C}_3\text{H}_7.\text{CO.Cl}$ , and upon butyric anhydride. It is further produced by a peculiar fermentation of glycerol, brought about in the presence of a schizomycetes (*Berichte*, 16, 1438). It is a liquid with an agreeable odor, has a sp. gr. of 0.8099 at  $20^\circ$  and boils at  $116.8$ . It is soluble at  $22^\circ$  in 12 volumes of water. Calcium chloride and other salts separate it again from its solution. When oxi-



dized it passes into butyl aldehyde and butyric acid. Its chloride,  $C_3H_7.CH_2Cl$ , boils at  $77.6^\circ$ , the bromide at  $99.8^\circ$ , and the iodide at  $120^\circ$ .

**Trichlorbutyl Alcohol**,  $(CH_3.CCl_2.CCl_2.CH_2.OH)$ , results when zinc ethyl and butyl chloral (see Trichlor-ethyl alcohol, p. 96) are brought together. It crystallizes in prisms, fuses at  $62^\circ$ , and boils under 45 mm. pressure at  $120^\circ$ . If oxidized with nitric acid it yields trichlorbutyric acid (*Annalen*, **213**, 374).

(2) **Isobutyl Alcohol**,  $C_3H_7.CH_2.OH$ , butyl alcohol of fermentation, occurs in several fusel oils and especially in the spirit from potatoes. It is a liquid possessing a fusel-oil odor, has a sp. gr. of 0.8020 at  $20^\circ$  and boils at  $108.4^\circ$ . It is soluble in ten parts of water, and is again separated from solution on the addition of salts. When oxidized it affords isobutyric acid. Its chloride,  $C_4H_9Cl$ , boils at  $69^\circ$ , the bromide at  $92^\circ$ , and the iodide at  $121^\circ$ . When the bromide is heated to  $240^\circ$  it is converted into tertiary butyl bromide; very probably  $(CH_3)_3C:CH_2$  forms at first, which subsequently yields  $(CH_3)_3CBr$  with  $HBr$  (p. 67).

When isobutyl alcohol is heated with  $HCl$ ,  $HBr$  or  $HI$  there result, in addition to the normal halogen esters, also those of trimethyl carbinol,  $(CH_3)_3CX$ , because isobutylene,  $(CH_3)_2C:CH_2$ , is produced from the former, and this then combines with the halogen hydrides to compounds of the type  $(CH_3)_2CX.CH_3$  (see p. 92).

(3) **Methyl-ethyl Carbinol**,  $\begin{array}{c} CH_3 \\ | \\ C_2H_5 \end{array} > CH.OH$  (Butylene Hydrate), is obtained

from its iodide, produced by heating erythrite with hydriodic acid (p. 67); the same iodide is also formed from normal butylene (pp. 58 and 92). The alcohol may further be made by treating formic ester with  $Zn$  and  $CH_3I$  and  $C_2H_5I$ ; and from the dichlor-ether,  $CH_2Cl.CHClO.C_2H_5$ , (see Ether) by the action of zinc-ethyl and  $HI$ . It is a strongly smelling liquid, boiling at  $98^\circ$ – $100^\circ$ . Its sp. gr. at  $0^\circ$  is 0.827. Heated to  $240^\circ$ – $250^\circ$  it decomposes into water and  $\beta$  butylene,

$CH_3.CH:CH.CH_3$ . It gives methyl-ethyl ketone,  $\begin{array}{c} CH_3 \\ | \\ C_2H_5 \end{array} > CO$ , when oxidized.

Its *iodide* boils at  $119$ – $120^\circ$ .

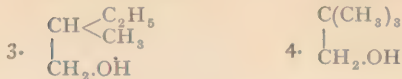
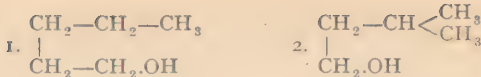
(4) **Trimethyl Carbinol**,  $(CH_3)_3C.OH$ , tertiary butyl alcohol, is found in slight quantity in fusel oil, and arises in the action of acetyl chloride upon zinc methyl (p. 90). It can also be obtained from the butyl alcohol of fermentation by means of isobutylene (p. 92).

When perfectly anhydrous it crystallizes in rhombic prisms or plates, fusing at  $28^\circ$  and boiling at  $83$ – $84^\circ$ . Its sp. gr. at  $30^\circ$  is 0.7788. It is miscible with water in all proportions, forming an hydrate ( $2C_4H_{10}O + H_2O$ ) which crystallizes in a freezing mixture and boils at  $80^\circ$ . When oxidized with chromic acid it yields carbon dioxide, acetic acid, acetone, and a little isobutyric acid.

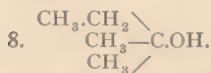
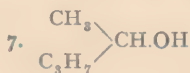
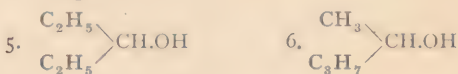
Its chloride,  $C_4H_9Cl$ , boils at  $50^\circ$ – $51^\circ$ , and the iodide at  $99^\circ$ . When the latter is heated with zinc and water trimethyl methane,  $C_4H_{10}$ , and isobutylene,  $C_3H_8 = (CH_3)_2C:CH_2$ , result. On combining the latter with  $ClOH$ ,  $(CH_3)_2CCl.CH_2.OH$  will be formed, from which, through the agency of nascent hydrogen, isobutyl alcohol,  $(CH_3)_2CH.CH_2.OH$ , is obtained.

5. **Amyl Alcohols**,  $C_5H_{11}.OH$ . Theoretically 8 isomerides are possible: 4 primary alcohols, 3 secondary, and 1 tertiary:—

Primary :



Secondary :



Tertiary :

(1) **Normal Amyl Alcohol**,  $\text{C}_4\text{H}_9\cdot\text{CH}_2\cdot\text{OH}$  (contains the normal butyl group), is obtained from valeraldehyde and from normal pentane. It is almost insoluble in water, has a fusel-oil odor, and boils at  $137^\circ$ . Its sp. gr. at  $20^\circ$  equals 0.8168. On oxidation it yields normal valeric acid. Its *chloride* boils at  $106-107^\circ\text{C}$ .; it is produced (together with  $\text{C}_3\text{H}_7\cdot\text{CHCl}\cdot\text{CH}_3$ ) in the chlorination of normal pentane. The bromide boils at  $129^\circ$ , and the iodide at  $155.5^\circ$ .

(2) **Isobutyl Carbinol**,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  (Inactive amyl alcohol, isopentyl alcohol), constitutes the chief ingredient of the amyl alcohol of fermentation obtained from fusel oil (p. 95) and occurs as esters of angelic and tiglic acids in Roman camomile oil. It may be obtained in a pure condition by synthesis from isobutyl alcohol,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ , by converting the latter into the cyanide, the acid, the aldehyde, and finally into the alcohol. It boils at  $131.4^\circ$ , and its sp. gr. at  $20^\circ$  is 0.8104. At  $13^\circ$  it dissolves in 50 parts water. Its chloride,  $\text{C}_5\text{H}_{11}\text{Cl}$ , boils at  $100^\circ$ , the bromide at  $120.4^\circ$ , and the iodide at  $148^\circ$ . When oxidized it yields valeric acid.

The so-called alcohol of fermentation, possessing a disagreeable odor and boiling at  $129-130^\circ$ , occurs in fusel oil and consists mainly of inactive isobutyl carbinol. In addition, methyl-ethyl carbinol (active amyl alcohol) and probably, too, normal amyl alcohol are present. It rotates the plane of polarization to the left; its activity is due to the presence of active amyl alcohol. The latter distils over first when fusel oil is thus treated.

Fermentation amyl-alcohol, treated with sulphuric acid, yields two amyl-sulphuric acids. The different solubilities and crystalline forms of their barium salts distinguish them. From the more difficultly soluble salt, which forms in rather large quantity, isobutyl carbinol may be obtained by boiling its acid with water. Active amyl alcohol is prepared from the more readily soluble salt. The first alcohol affords inactive valeric acid on oxidation, the second the active acid.

An easier separation of the alcohols is reached by conducting HCl into the mixture. Isobutyl carbinol will be etherified first, the active amyl alcohol remaining (Le Bel). When the crude fermentation alcohol is distilled with zinc chloride ordinary amylene is the product. This consists mainly of  $(\text{CH}_3)_2\text{C}:\text{CH}.\text{CH}_3$ , resulting from a transposition of isobutyl carbinol; it contains, besides,  $\gamma$ -amylene and  $\alpha$ -amylene (compare p. 58). The iodide of the fermentation alcohol is

made up principally of  $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_2\text{I}$  and  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{matrix} \text{CH}.\text{CH}_2\text{I}$ , and yields

the amylenes,  $(\text{CH}_3)_2\text{CH}:\text{CH}:\text{CH}_2$  and  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{matrix} \text{C}:\text{CH}_2$  (page 59).

(3) **Active Amyl Alcohol**,  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{matrix} \text{CH}.\text{CH}_2.\text{OH}$ , secondary butyl carbinol,

methyl-ethyl carbinol, is the active ingredient (about 13 per cent.) of the fermentation alcohol, and may be separated from this by the method above described. It boils at  $127^\circ$ . In accordance with its asymmetric structure (p. 47) it is optically inactive and is indeed *laevo*-rotatory  $[\alpha]_D = 4.4^\circ$ . Its chloride,  $\text{C}_5\text{H}_{11}\text{Cl}$ , boils from  $97$ – $99^\circ$ , the bromide from  $117$ – $120^\circ$ , and the iodide from  $144$ – $145^\circ$ . These are all optically active. The same may be noted in regard to ethyl amyl and diamyl obtained from the iodide. Those derivatives, on the contrary, not containing an asymmetric carbon atom, are inactive, *e. g.*, amyl

hydride,  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{matrix} \text{CH}.\text{CH}_3$ , and  $\gamma$ -amylene,  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{matrix} \text{C}:\text{CH}_2$  (p. 42 and *Annalen*,

220, 157). Active valeric acid,  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{matrix} \text{CH}.\text{CO}_2\text{H}$ , results from the oxidation of amyl alcohol.

Active amyl alcohol becomes inactive on boiling with NaOH, otherwise it manifests all the properties of the active modification. A mucor will render it again active, but *dextro*-rotatory (*Berichte*, 15, 1506).

(4) **Tertiary Butyl Carbinol**,  $(\text{CH}_3)_3\text{C}.\text{CH}_2.\text{OH}$ , has not been obtained as yet, but no doubt may be prepared from tertiary butyl alcohol through the cyanide (as in the case of isobutyl carbinol).

(5) **Diethyl Carbinol**,  $(\text{C}_2\text{H}_5)_2\text{CH}.\text{OH}$ , is formed by the action of zinc and ethyl iodide upon ethyl formate (p. 91). It boils at  $116$ – $117^\circ$ , and has a specific gravity at  $0^\circ$  of 0.832. Its iodide boils at  $145^\circ$ , and the acetate at  $132^\circ$ ,  $\beta$ -amylene (p. 59) is obtained from the iodide. Diethyl ketone,  $(\text{C}_2\text{H}_5)_2\text{CO}$ , results from the oxidation of the alcohol. Since  $\beta$ -amylene,  $\text{C}_2\text{H}_5.\text{CH}:\text{CH}.\text{CH}_3$ , yields  $\text{C}_2\text{H}_5.\text{CH}_2.\text{CH}:\text{CH}_3$  with  $\text{HI}$ , from which methyl normal propyl carbinol is obtained, we can in this manner convert the diethyl carbinol into the latter alcohol.

(6) **Methyl Normal Propyl Carbinol**,  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}_8\text{H}_7 \end{matrix} \text{CH}.\text{OH}$ , is formed from methyl

propyl ketone by the action of nascent hydrogen. It may be obtained, too, from the iodide,  $\text{C}_8\text{H}_7.\text{CHI}.\text{CH}_3$  (from  $\alpha$ - and  $\beta$ -amylene, see above), and the chloride,  $\text{C}_8\text{H}_7.\text{CHCl}.\text{CH}_3$  (from normal pentane). It boils at  $118.5^\circ$ . Its sp. gr. at  $0^\circ$  is 0.824. Its iodide boils at  $144$ – $145^\circ$ , and the chloride at  $103$ – $105^\circ$ . Methyl normal propyl ketone is the oxidation product of the alcohol. The iodide yields  $\beta$ -amylene.

(7) **Methyl Isopropyl Carbinol**,  $\begin{matrix} \text{CH}_3 \\ | \\ \text{C}_3\text{H}_7 \end{matrix} \text{CH.OH}$ , is obtained by the action of sodium amalgam upon an aqueous solution of the corresponding ketone. It is an oil with a fusel odor, boils at  $112.5^\circ$ , and has a sp. gr. at  $0^\circ$  of 0.833. When oxidized it yields methyl isopropyl ketone.

When acted upon by halogen hydrides and also  $\text{PCl}_3$ , the derivatives of the type,  $\begin{matrix} \text{CH}_3 \\ | \\ \text{C}_3\text{H}_7 \end{matrix} \text{CHX}$ , do not form, but, in a singular manner, those of tertiary amyl alcohol:—



Very probably amylene,  $(\text{CH}_3)_2\text{C}:\text{CH}.\text{CH}_3$ , is the first product, and this by addition of the halogen hydrides yields the derivatives of tertiary amyl alcohol (compare p. 92).

The real derivatives of methyl isopropyl carbinol are afforded by  $\alpha$ -isoamylene,  $(\text{CH}_3)_2\text{CH}.\text{CH}:\text{CH}_2$  (p. 59), by the addition of halogen hydrides at ordinary temperatures or when warmed. The resulting iodide,  $(\text{CH}_3)_2\text{CH}.\text{CHI}.\text{CH}_3$ , boils at  $137-139^\circ$ , the bromide, at  $114-116^\circ$ , and the chloride at  $91^\circ$ . The iodide yields  $\beta$ -isoamylene,  $(\text{CH}_3)_2\text{C}:\text{CH}.\text{CH}_3$ .

(8) **Tertiary Amyl Alcohol**,  $\begin{matrix} (\text{CH}_3)_2 \\ | \\ \text{C}_2\text{H}_5 \end{matrix} \text{C.OH}$ , Dimethyl-ethyl-carbinol, Amylene hydrate. This is synthetically prepared by the action of zinc methyl on propionyl chloride. It may be obtained from  $\gamma$ -amylene,  $\begin{matrix} \text{CH}_3 \\ | \\ \text{C}_2\text{H}_5 \end{matrix} \text{C}:\text{CH}_2$ , and

$\beta$ -isoamylene,  $(\text{CH}_3)_2\text{C}:\text{CH}.\text{CH}_3$ , when their HI compounds are heated with lead oxide and water. Since ordinary amylene consists chiefly of  $\beta$ -isoamylene (p. 59), tertiary amyl alcohol is most practically prepared from the first by shaking it with sulphuric acid and boiling the solution with water (*Annalen*, 190, 345).

Tertiary amyl alcohol has an odor like that of camphor, boils at  $102.5^\circ$ , solidifies at  $-12.5^\circ$  and melts at  $-12^\circ$ . Its specific gravity at  $0^\circ$  is 0.827. Its iodide boils at  $127-128^\circ$ , the bromide at  $108-109^\circ$ , and the chloride at  $86^\circ$ . At  $200^\circ$  it decomposes into water and  $\beta$ -isoamylene. Acetic acid and acetone are its oxidation products.

6. **Hexyl and Caproyl Alcohols**,  $\text{C}_6\text{H}_{13}.\text{OH}$ . Seventeen isomerides are theoretically possible: 8 primary (as there are eight amyl radicals), 6 secondary, and 3 tertiary. Of the eight known at present there may be mentioned:—

(1) **Normal Hexyl Alcohol**,  $\text{CH}_3.(\text{CH}_2)_4.\text{CH}_2.\text{OH}$ . This was first obtained (together with methyl butyl carbinol) from normal hexane. It can be prepared pure from caproic acid,  $\text{C}_6\text{H}_{12}\text{O}_2$ , by reduction, and by the transformation of hexylamine (from cœnanthyllic acid,  $\text{C}_7\text{H}_{14}\text{O}_2$ , *Berichte*, 16, 744). Hexyl butyrate occurs in the volatile products of some *Heracleum* varieties (together with octyl acetate). The alcohol may be obtained from these by saponification with caustic potash. It boils at  $157^\circ$ , and has a specific gravity at  $23^\circ$  of 0.819. Normal caproic acid is its oxidation product. The iodide,  $\text{C}_6\text{H}_{13}\text{I}$ , boils at  $180^\circ$ , and the chloride,  $\text{C}_6\text{H}_{13}\text{Cl}$ , at  $130-133^\circ$ .

(2) **Methyl-tertiary Butyl Carbinol**,  $(\text{CH}_3)_3.\text{C}.\text{CH.OH}.\text{CH}_3$ , Pinacolyl alcohol. Nascent hydrogen acting on pinacoline (see this) affords the above alcohol. When cooled it crystallizes and melts at  $-4^\circ$ . It boils at  $120^\circ$ , and has a specific gravity of 0.834. If oxidized with a chromic acid mixture it first



yields the ketone,  $\begin{array}{c} (\text{CH}_3)_3\text{C} \\ \text{CH}_3 \end{array} \text{CO}$ , *pinacolone*; subsequently this breaks up into carbon dioxide and trimethyl acetic acid.

(3) **Fermentation Hexyl Alcohol** or **Caproyl Alcohol**,  $\text{C}_6\text{H}_{13}\text{OH}$ , is found in the fusel oil of grape spirit. It boils at  $150^\circ$ . Its constitution is not well determined. That it is a primary alcohol is evident from the fact that when oxidized caproic acid results.

7. **Heptyl or Cœnanthyl Alcohols**,  $\text{C}_7\text{H}_{15}\text{OH}$ . Thirteen of the thirty-eight possible isomerides are known. The following may be noticed:—

(1) **Normal Heptyl Alcohol**,  $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$ , from cœnanthyl aldehyde and normal heptane, boils at  $175^\circ$  and yields normal cœnanthylic acid on oxidation.

(2) **Dimethyl-tertiary Butyl Carbinol**,  $\text{C}(\text{CH}_3)_3\text{C}(\text{CH}_3)_2\text{OH}$ , or Penta-methyl-ethyl alcohol, obtained from trichlor-methyl acetic anhydride,  $\text{C}(\text{CH}_3)_3\text{COCl}$ , by means of zinc methyl, melts at  $+17^\circ$  and boils at  $131\text{--}132^\circ$ . It affords a crystalline hydrate,  $2\text{C}_7\text{H}_{16}\text{O} + \text{H}_2\text{O}$ , with water. This melts at  $83^\circ$ . Its chloride boils at  $136^\circ$ , and the iodide at  $141^\circ$ .

The following higher normal alcohols are known. Octyl, cetyl, ceryl, and melissyl alcohols occur naturally as esters; the others are obtained from the corresponding aldehydes by reduction (p. 90).

**Octyl Alcohol**,  $\text{C}_8\text{H}_{18}\text{O}$ , occurs as octyl acetate in the volatile oil of *Heracleum spondylium*, as butyrate in the oil of *Pastinaca sativa*, and together with hexyl butyrate in the oil from *Heracleum giganteum*. It boils at  $190\text{--}192^\circ$ , and at  $16^\circ$  it has a sp. gr. = 0.830. Caprylic acid is its oxidation product.

**Decyl Alcohol**,  $\text{C}_{10}\text{H}_{22}\text{OH}$ , from capric aldehyde, melts at  $-7^\circ$ , and under 15 mm. pressure boils at  $119^\circ$ .

**Dodecatyl Alcohol**,  $\text{C}_{12}\text{H}_{26}\text{OH}$ , from lauraldehyde, melts at  $24^\circ$ , and boils at  $143.5^\circ$  under a pressure of 15 mm.

**Tetradecatyl Alcohol**,  $\text{C}_{14}\text{H}_{29}\text{OH}$ , from myristaldehyde, melts at  $32^\circ$ , and under a pressure like that given with the preceding compounds boils at  $167^\circ$ .

**Cetyl Alcohol**,  $\text{C}_{16}\text{H}_{33}\text{OH}$ , formerly called *ethal*, is prepared from the cetyl ester of palmitic acid, the chief ingredient of spermaceti, by saponification with alcoholic potash:—

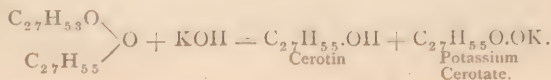


It may also be obtained by the reduction of palmitic aldehyde.

Ethal is a white, crystalline mass fusing at  $49.5^\circ$ , and distilling about  $340^\circ$  with scarcely any decomposition (under 15 mm. pressure it boils at  $189^\circ$ ). When fused with potassium hydroxide it yields palmitic acid.

**Octodecyl Alcohol**,  $\text{C}_{18}\text{H}_{37}\text{OH}$ , from stearaldehyde, fuses at  $59^\circ$ , and boils at  $210^\circ$  (under 15 mm.).

**Ceryl Alcohol**,  $\text{C}_{27}\text{H}_{55}\text{OH}$ —*Cerotin*—as ceryl cerotic ester constitutes Chinese wax. It is obtained by melting the latter with caustic potash:—



Ceryl alcohol is a white, crystalline mass, fusing at  $79^{\circ}$ . It yields cerotic acid when fused with KOH.

**Melissyl Alcohol**,  $C_{30}H_{61}.OH$ , myricyl alcohol, occurs as myricyl palmitate in beeswax. It is isolated in the same manner as the preceding compound, and melts at  $85^{\circ}$ . Its chloride melts at  $64^{\circ}$ , and the iodide at  $69.5^{\circ}$ .

## 2. UNSATURATED ALCOHOLS, $C_nH_{2n-1}.OH$ .

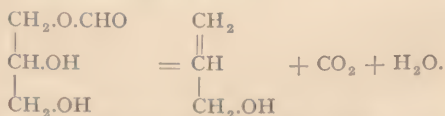
These are derived from the unsaturated alkylens,  $C_nH_{2n}$ , in the same manner as the normal alcohols are obtained from their hydrocarbons. In addition to the general character of alcohols they possess also the capability of directly binding two additional affinities.

The lowest member of the series—the so-called *vinyl alcohol*— $C_2H_3.OH = CH_2:CH.OH$ , does not appear to exist, because in all the reactions in which it should form, the isomeric acetaldehyde,  $CH_3.CHO$ , is produced. It seems to be the universal rule, that the atomic grouping  $-C:CH.OH$  in the act of formation is transposed into  $-CH.CHO$ , as aldehydes result instead of the expected secondary alcohols. The group  $C.C(OH):CH_2$  (with tertiary alcohol group) passes over into  $C.CO.CH_3$ , since ketones are always produced (compare acetone). These facts explain many abnormal reactions (compare *Berichte*, 13, 309, and 14, 320). The same rule holds good for the unsaturated oxy-acids in free condition, but does not apply to their salts and esters (*Berichte*, 16, 2824).

**1. Allyl Alcohol**,  $C_3H_5.OH = CH_2:CH.CH_2.OH$ . This may be prepared by heating allyl iodide to  $100^{\circ}$  (p. 71) with 20 parts water. It is produced, also, when nascent hydrogen acts upon acrolein,  $CH_2:CH.CO.H$ , and sodium upon dichlorhydrin,  $CH_2Cl.CHCl.CH_2.OH$ . It is best prepared from glycerol by heating the latter with formic or oxalic acid.

*Preparation.*—A mixture of 4 parts glycerol and 1 part crystallized oxalic acid, with addition of  $\frac{1}{2}$  per cent. ammonium chloride, is slowly heated to  $100^{\circ}$  in a retort. Carbon dioxide is disengaged, while formic acid and some allyl alcohol pass over. When the liberation of gas has ceased somewhat, the heat is raised to  $200^{\circ}$ , and the distillate collected. The latter contains, besides allyl alcohol, some allyl formate and acrolein. To further purify it the distillation is repeated, the product warmed with KOH and dehydrated by distillation over barium oxide (*Annalen*, 167, 222).

In this reaction the oxalic acid at first breaks up into carbon dioxide and formic acid, which forms an ester with the glycerol; this then decomposes into allyl alcohol, carbon dioxide, and water:—



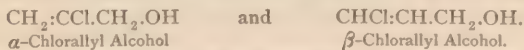
By this method 20–25 per cent. of the glycerol is changed to allyl alcohol.

Allyl alcohol is a mobile liquid with a pungent odor, boiling at  $96-97^\circ$ , and having at  $20^\circ$  a specific gravity of 0.8540. It solidifies at  $-50^\circ$ . It is miscible with water and burns with a bright flame.

It yields acrolein and acrylic acid when oxidized with silver oxide, and only formic acid (no acetic) when chromic acid is the oxidizing agent. Nascent hydrogen is apparently without effect upon it; when heated to  $150^\circ$  with KOH formic acid, normal propyl alcohol and other products are obtained.

For the halogen esters of allyl alcohol see page 70.

It combines with  $\text{Cl}_2$  and  $\text{Br}_2$  to form the  $\beta$ -dichlorhydrins of glycerol (see this). The monosubstituted allyl alcohols are represented by two isomerides:—



The first of these is formed from  $\alpha$ -dichlorpropylene,  $\text{CH}_2:\text{CCl}.\text{CH}_2\text{Cl}$ , on boiling with a sodium carbonate solution; it boils at  $136^\circ$ . When it is dissolved in sulphuric acid and distilled with water it becomes acetone alcohol,  $\text{CH}_3.\text{CO}.\text{CH}_2.\text{OH}$ .

$\beta$ -Chlorallyl Alcohol, from  $\beta$ -dichlorpropylene,  $\text{CHCl}:\text{CH}.\text{CH}_2\text{Cl}$ , boils at  $153^\circ$ , and causes painful blisters.

$\beta$ -Bromallyl Alcohol,  $\text{CHBr}:\text{CH}.\text{CH}_2.\text{OH}$ , from  $\beta$ -dibrompropylene, boils at  $152^\circ$ , and yields propargylic alcohol with KOH.

2. Crotyl Alcohol,  $\text{C}_4\text{H}_7.\text{OH} = \text{CH}_3.\text{CH}:\text{CH}.\text{CH}_2.\text{OH}$ , is obtained from crotonaldehyde by means of nascent hydrogen. It boils at  $117-120^\circ$ .

3. Higher unsaturated alcohols of the allyl series, having tertiary structure, arise in the action of zinc and allyl iodide upon ketones and in the decomposition of the resulting product with water (p. 91).

### (3) UNSATURATED ALCOHOLS, $\text{C}_n\text{H}_{2n-3}.\text{OH}$ .

The only known alcohol of the acetylene series in which there exists triple union of two carbon atoms is **Propargyl Alcohol**,  $\text{C}_3\text{H}_4\text{O} = \text{CH}:\text{C}.\text{CH}_2.\text{OH}$ , which is derived from  $\beta$ -bromallyl alcohol (see above) on heating it with KOH and some water:—



Propargyl alcohol (or propinyl alcohol) is a mobile, agreeable-smelling liquid, with a sp. gr. at  $20^\circ$  of 0.9715. It boils at  $114-115^\circ$ , and dissolves readily in water. With an ammoniacal cuprous chloride solution (p. 61) it gives a yellow precipitate,  $(\text{C}_3\text{H}_2.\text{OH})_2\text{Cu}_2$ , from which the alcohol is again set free by acid. Silver solutions produce a white precipitate,  $\text{C}_3\text{H}_2\text{Ag}.\text{OH}$ .

Trichloride of phosphorus converts the alcohol into the chloride,  $\text{C}_3\text{H}_3\text{Cl}$ . This boils at  $65^\circ$ . The bromide,  $\text{C}_3\text{H}_3\text{Br}$ , formed by  $\text{PBr}_3$ , boils at  $88-90^\circ$ ; the iodide boils at  $48-49^\circ$ . The acetate,  $\text{C}_3\text{H}_3.\text{O}.\text{C}_2\text{H}_5\text{O}$ , results when acetyl chloride acts upon the alcohol. Its boiling point is  $125^\circ$ .

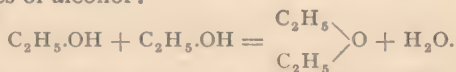
**Ethyl-Propinyl Ether**,  $\text{C}_3\text{H}_3.\text{O}.\text{C}_2\text{H}_5$ , is made from glyceryl bromide,  $\text{C}_3\text{H}_5\text{Br}_3$ , and the various dichlor- and dibrom-propylenes,  $\text{C}_3\text{H}_4\text{Br}_2$ , by the aid of alcoholic potash. It is a liquid with a penetrating odor, of sp. gr. 0.8320

at 20°, and boils at 80°. Its copper compound,  $(C_3H_7.O.C_2H_5)_2Cu$ , is yellow colored, while that with silver,  $C_3H_7Ag.O.C_2H_5$ , is white.

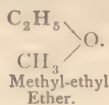
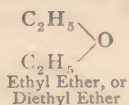
Higher alcohols, in which the double union of carbon atoms occurs twice, are produced by the action of zinc and allyl iodide upon ethers of formic acid and even of acetic acid, whereby secondary and tertiary alcohols result (p. 91). These alcohols absorb four bromine atoms, but do not, however, enter into combination with copper and silver. This accords with their structure.

## ETHERS.

The oxides of the alcohol radicals are thus designated. In the ethers of the monohydric alcohols two alkyls are present, joined to each other by an oxygen atom. They may be considered also as anhydrides of the alcohols, formed by the elimination of water from two molecules of alcohol:—



Ethers containing two similar alcohol radicals are termed *simple ethers*; those with different radicals, *mixed ethers*:—



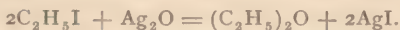
We must make a distinction between the above and the so-called compound ethers or *esters*, in which both an alcohol radical and an acid radical are present, *e. g.*,—



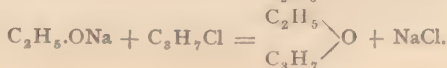
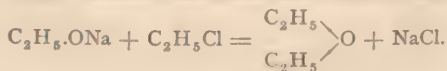
The properties of these are entirely different from those of the alcohol ethers. In the following pages they will always be termed *esters*.

The following are the most important methods of preparing ethers:—

1. Action of the alkylogens upon metallic oxides, especially silver oxide:—

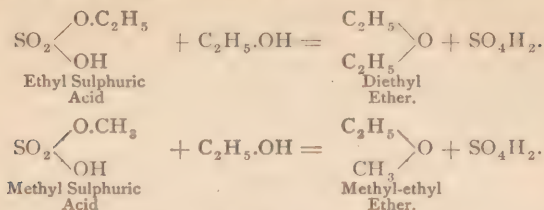


2. The action of the alkylogens upon the sodium alcoholates in alcoholic solution. Mixed ethers are also formed here:—

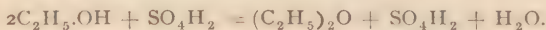




## 3. Heating the sulphuric esters with alcohols :—



The formation of ethers by directly heating the alcohols with sulphuric acid is based on this reaction :—

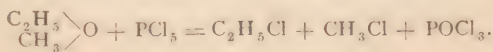


By mixing and warming alcohol with sulphuric acid, a sulphuric ester (together with water) is produced (p. 89). With excess of alcohol, on application of heat, this breaks up into ether and sulphuric acid. The ether and water distil over while the sulphuric acid remains behind. If a new portion of alcohol be added to this residue the process repeats itself. In this way, an unlimited amount of alcohol can be changed to ether by one and the same quantity of sulphuric acid, providing the latter does not sustain a slight and otherwise different transposition. Formerly this process, when the mechanism of the reaction was yet unexplained, was included in the category of *catalytic* actions. The explanation of the etherification process (by Williamson, in 1852) marks an important turning point in the history of chemistry.

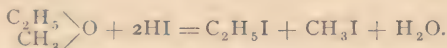
When a mixture of two alcohols is permitted to act upon sulphuric acid, three ethers are simultaneously formed; two are simple and one a mixed ether. Other polybasic acids, like phosphoric, arsenic, and boric, behave like sulphuric acid.

Ethers are neutral, volatile bodies, nearly insoluble in water. The lowest members are liquid; the highest, *e. g.*, cetyl ether, are solids. Their boiling points lie markedly lower than those of the corresponding alcohols.

Chemically, ethers are very indifferent, because all the hydrogen is attached to carbon. When oxidized they yield the same products as their alcohols. Heated with concentrated sulphuric acid they afford ethereal salts. Phosphorus chloride converts them into alkyl chlorides :—



The same occurs when they are heated with the haloid acids, especially with HI:—



When acted upon by HI in the cold, they decompose into alcohol and an iodide. With mixed ethers it is the iodide of the lower radical that is invariably produced (*Berichte*, 9, 852):—



Many ethers, especially those with secondary and tertiary alkyls and those with unsaturated alkyls, break up into alcohols (*Berichte*, 10, 1903), when heated with water or dilute sulphuric acid to 150°.

**Methyl Ether**,  $(\text{CH}_3)_2\text{O}$ , is prepared by heating methyl alcohol with sulphuric acid. It is an agreeable-smelling gas, which may be condensed to a liquid at about — 23°. Water dissolves 37 volumes and sulphuric acid upwards of 600 volumes of the gas.

In preparing it 4 parts methyl alcohol and 6 parts concentrated sulphuric acid are heated to 140°, in a flask, in connection with a return condenser. The liberated gas is purified by conducting it through potash. (*Berichte*, 7, 699.)

Substitution products form when chlorine is allowed to act gradually:  $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_3$  boils at 60°,  $(\text{CH}_2\text{Cl})_2\text{O}$  boils at 105°, and at last perchlormethyl ether,  $(\text{CCl}_3)_2\text{O}$ , which decomposes about 100°.

**Ethyl Ether**,  $(\text{C}_2\text{H}_5)_2\text{O}$ , is prepared by heating ethyl alcohol with sulphuric acid (p. 106).

A mixture of 5 parts (80–90 per cent.) alcohol and 9 parts  $\text{H}_2\text{SO}_4$  is warmed in a flask connected with a condenser. A thermometer passes through the cork of the vessel and dips into the liquid. When the temperature has reached 140°, a slow stream of alcohol is allowed to enter the flask through a tube leading into the latter. The temperature given must be maintained. The ethyl sulphuric acid produced at the beginning reacts at 140° upon the entering alcohol forming sulphuric acid and ether, which regularly distils over with the water formed in the reaction. The distillate is a mixture of ether, water, and some alcohol. It is shaken with soda, to combine sulphurous acid, the lighter layer of ether is siphoned off and distilled over lime. There is always some alcohol in the product. To remove this entirely distil repeatedly over sodium, until hydrogen is no longer evolved. Any water in the ether may be detected by shaking the latter with an equal volume of  $\text{CS}_2$ , when a turbidity will ensue. To detect alcohol, ether is agitated with aniline violet. When the former is absent the ether remains uncolored.

Ethyl ether is a mobile liquid with peculiar odor and specific gravity at 0° of 0.736. Anhydrous, it does not congeal at — 80°. It boils at 35° and evaporates very rapidly even at medium temperatures. It dissolves in 10 parts water and is miscible with alcohol. Nearly all the carbon compounds insoluble in water,

such as the fats and resins, are soluble in ether. It is extremely inflammable, burning with a luminous flame. Its vapor forms a highly explosive mixture with air. When inhaled, ether vapor brings about unconsciousness. *Hoffmann's Anodyne* is a mixture of 3 parts alcohol and 1 part ether.

Ether unites with bromine to form peculiar, crystalline addition products, somewhat like bromine hydrate; it combines, too, with water and metallic salts. When heated with water and sulphuric acid to  $180^{\circ}$  ethyl alcohol results. Chlorine acting upon cooled ether forms various substitution products: monochlorether,  $\text{CH}_3\cdot\text{CHCl}\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , boiling point  $98^{\circ}$ , dichlorethyl oxide,  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , boiling point  $145^{\circ}$  and higher derivatives. An isomeric dichlorether,  $(\text{CH}_3\cdot\text{CHCl})_2\text{O}$ , is produced when  $\text{HCl}$  acts upon aldehyde. It boils at  $116^{\circ}$ . *Perchlorinated Ether*,  $(\text{C}_2\text{Cl}_5)_2\text{O}$ , the last product of the action of chlorine on ethyl oxide, is a crystalline body, fusing at  $68^{\circ}$  and decomposing upon distillation into  $\text{C}_2\text{Cl}_6$  and trichloroacetyl chloride,  $\text{C}_2\text{Cl}_5\cdot\text{O}\cdot\text{Cl}$ .

When ozone is conducted into anhydrous ether, a thick liquid, having the composition  $\text{C}_8\text{H}_{20}\text{O}_3$ , is formed. This explodes on being heated. It is considered an ethyl peroxide,  $(\text{C}_2\text{H}_5)_4\text{O}_3$ . Water converts it into alcohol and hydrogen peroxide.

**Methyl Ethyl Ether**,  $\text{CH}_3\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , boils at  $11^{\circ}$ . **Methyl Propyl Ether**,  $\text{CH}_3\cdot\text{O}\cdot\text{C}_3\text{H}_7$ , at  $50^{\circ}$ .

**Normal Propyl Ether**,  $(\text{C}_3\text{H}_7)_2\text{O}$ , boils at  $86^{\circ}$ . **Isopropyl Ether**, from isopropyl iodide, boils at  $60-62^{\circ}$ .

**Isomyl Ether**,  $(\text{C}_5\text{H}_{11})_2\text{O}$ , is formed together with amylene, and its polymerides when fermentation amyl alcohol is heated with sulphuric acid. It boils at  $176^{\circ}$ , and has a specific gravity of 0.779.

**Cetyl Ether**,  $(\text{C}_{16}\text{H}_{33})_2\text{O}$ , from cetyl iodide, crystallizes from ether in brilliant leaflets, fuses at  $55^{\circ}$ , and boils at  $300^{\circ}$ .

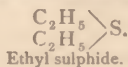
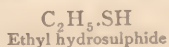
**Allyl Ether**,  $(\text{C}_3\text{H}_5)_2\text{O}$ , from allyl iodide, boils at  $85^{\circ}$ .

**Vinyl Ethyl Ether**,  $\text{C}_2\text{H}_3\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , is produced when chloroacetal,  $\text{CH}_2\text{Cl}\cdot\text{CH}\cdot(\text{O}\cdot\text{C}_2\text{H}_5)_2$ , (obtained from acetal by chlorination and from dichloro-ether,  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , by aid of sodium alcoholate) is heated with sodium. It is a liquid with an allyl-like odor, and boils at  $35.5^{\circ}$ . Chlorine added to it gives again dichlorether. When boiled with dilute sulphuric acid it decomposes into ethyl alcohol and aldehyde (p. 103).

**Allyl Ethyl Ether**,  $\text{C}_3\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , from allyl iodide and sodium ethylate, boils at  $66^{\circ}$ . It combines directly with  $\text{Br}_2$ ,  $\text{Cl}_2$  and  $\text{ClOH}$ .

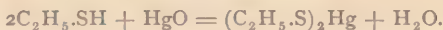
## MERCAPTANS AND THIO-ETHERS.

Just as the metallic oxides and hydroxides have their analogous sulphur compounds, so we find corresponding to the alcohols and ethers *thio-alcohols* or *mercaptans* and *thio-ethers* or *alkyl-sulphides* :—



Although in general they closely resemble the alcohols and ethers, the sulphur in them imparts additional specific properties. In the alcohols the H of OH is replaceable by alkali metals almost

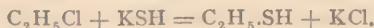
exclusively; in the mercaptans it can also be replaced by heavy metals (by action of metallic oxides). The mercaptans react very readily with mercuric oxide, whereby crystalline compounds result :—



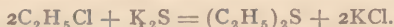
Hence their designation as mercaptans (from *Mercurium captans*).

The methods resorted to for their formation are perfectly analogous to those employed for the alcohols. They are produced :—

(1) By the action of the alkylogens upon potassium sulphhydrate in alcoholic solution :—



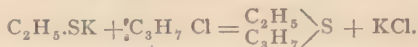
Similarly, the thio-ethers are formed by action of the alkylogens upon potassium sulphide :—



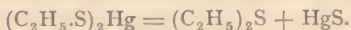
When polysulphides are employed instead of  $\text{K}_2\text{S}$ , polysulphides of the alcohol radicals, like  $\text{C}_2\text{H}_5\cdot\text{S}_2$ , are obtained.

Ethyl disulphide.

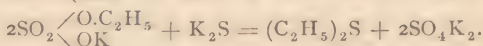
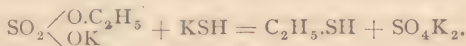
The alkyl sulphides are also produced when the alkylogens act upon the metallic compounds of the mercaptans. Mixed thio-ethers can also be made by this method :—



Further, they are produced when the mercury mercaptides are subjected to heat :—

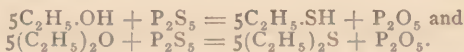


(2) By distilling salts of the sulphuric esters with potassium sulphhydrate or potassium sulphide (see p. 89) :—



The neutral esters of sulphuric acid, e.g.,  $\text{SO}_2(\text{O}\cdot\text{C}_2\text{H}_5)_2$  (p. 116), also yield mercaptans when heated with KSH.

(3) A direct replacement of the O of alcohols and ethers by S may be attained by phosphorus sulphide :—

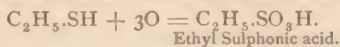


The  $\text{P}_2\text{O}_5$  is likely to react further upon the alcohols, and then phosphoric acid esters will appear simultaneously with the preceding compounds.

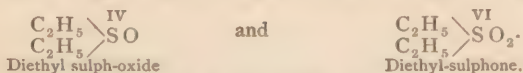
The mercaptans and thio-ethers are colorless liquids, for the most part insoluble in water, and possessed of a disagreeable, garlic-like odor. The alcoholic polysulphides are yellow-colored liquids. The metallic derivatives of the mercaptans—termed *mercaptides*—may be obtained by the double decomposition of the alkali compounds, and also by the direct action of the metallic oxides.



A solution of ferric chloride is colored deep red by all the mercaptans; the color soon disappears (*Berichte* 13, 44). When oxidized with nitric acid the mercaptans unite with three atoms of oxygen, and yield the so-called sulphonic acids (p. 119):—



The sulphur ethers, also, take up one and two sulphur atoms when treated with  $\text{HNO}_3$ , and yield *sulphoxides* and *sulphones*:—



These compounds may be compared to the ketones. Nascent hydrogen ( $\text{Zn}$  and  $\text{H}_2\text{SO}_4$ ) deoxidizes the sulphoxides to sulphides.

Some thio-compounds can be changed to the oxygen derivatives by the action of silver oxide:—



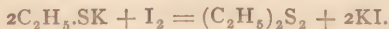
**Methyl Mercaptan**,  $\text{CH}_3\cdot\text{SH}$ , is a light liquid, that will swim on water, and boils at  $20^\circ$ . Methyl sulphide,  $(\text{CH}_3)_2\text{S}$ , boils at  $37.5^\circ$ , and combines with bromine to yield a crystalline compound,  $(\text{CH}_3)_2\text{SBr}_2$ . Concentrated nitric acid oxidizes methyl sulphide to sulphoxide,  $(\text{CH}_3)_2\text{SO}$ , which forms the salt  $(\text{CH}_3)_2\text{SO}\cdot\text{NO}_3\text{H}$  with an excess of acid. Barium carbonate separates the free sulphoxide from this. Silver oxide produces the same compound when it acts upon the bromide,  $(\text{CH}_3)_2\text{SBr}_2$ . The sulphoxide is an oil, soluble in water, and congealed by cold. On heating methyl sulphide with fuming nitric acid we obtain dimethyl-sulphone,  $(\text{CH}_3)_2\text{SO}_2$ . This is a crystalline body, fusing at  $109^\circ$ , and boiling at  $238^\circ$ .

**Ethyl Mercaptan**,  $\text{C}_2\text{H}_5\cdot\text{SH}$ , is a colorless liquid, boiling at  $36^\circ$ , and solidifying to a crystalline mass upon rapid evaporation. It is but slightly soluble in water; readily in alcohol and ether.

It may be prepared by saturating a concentrated  $\text{KOH}$  solution with hydrogen sulphide, adding potassium ethyl sulphate to this, and then distilling, when the light mercaptan will swim upon the aqueous distillate. To obtain it perfectly pure, shake with  $\text{HgO}$ , recrystallize the solid mercaptide from alcohol, and then decompose it with  $\text{H}_2\text{S}$ .

Mercury mercaptide,  $(\text{C}_2\text{H}_5\cdot\text{S})_2\text{Hg}$ , crystallizes from alcohol in brilliant leaflets, fusing at  $86^\circ$ , and is only slightly soluble in water. When mercaptan is mixed with an alcoholic solution of  $\text{HgCl}_2$  there is precipitated the compound  $\text{C}_2\text{H}_5\cdot\text{S}\cdot\text{HgCl}$ . The potassium and sodium compounds are best obtained by dissolving the metals in mercaptan diluted with ether; they crystallize in white needles.

The disulphides are produced when iodine acts upon the mercaptides:—



**Ethyl Sulphide**,  $(\text{C}_2\text{H}_5)_2\text{S}$ , obtained by the distillation of ethyl chloride with an alcoholic solution of  $\text{K}_2\text{S}$ , boils at  $91^\circ$ . It combines with some metallic chlorides to yield double compounds, like  $(\text{C}_2\text{H}_5)_2\text{S}\cdot\text{HgCl}_2$  and  $[(\text{C}_2\text{H}_5)_2\text{S}]_2\cdot\text{PtCl}_4$ .

If oxidized with dilute nitric acid it forms the sulphoxide,  $(C_2H_5)_2SO$ , an oily liquid, which decomposes when distilled. Fuming nitric acid produces diethyl sulphone,  $(C_2H_5)_2SO_2$ , soluble in water and alcohol, and crystallizing in large, colorless plates. It melts at  $70^\circ$ , and boils, undecomposed, at  $248^\circ$ . Nascent hydrogen (zinc and sulphuric acid) converts the sulphoxide into ethyl sulphide.

*Propyl Mercaptan*,  $C_3H_7.SH$ , boils at  $68^\circ$ , and the iso-derivative at  $58-60^\circ$ .  
*Dipropyl sulphide*,  $(C_3H_7)_2S$ , boils at  $130-135^\circ$ .

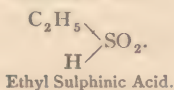
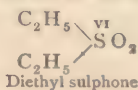
*Normal Butyl Mercaptan*,  $C_4H_9.SH$ , boils at  $98^\circ$ ; dibutyl sulphide at  $182^\circ$ ; di-isobutyl sulphide at  $173^\circ$ . The latter yields only one monoxide with nitric acid, while a dioxide is also obtained from dibutyl sulphide (*Annalen* 175, 349).

*Cetyl Sulphide*,  $(C_{16}H_{33})_2S$ , crystallizes in shining leaflets, fusing at  $57^\circ$ .

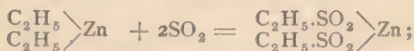
**Allyl Mercaptan**,  $C_3H_5.SH$ , is very similar to ethyl mercaptan, and boils at  $90^\circ$ .

**Allyl Sulphide**,  $(C_3H_5)_2S$ , is the chief constituent of the oil of garlic (from *Allium sativum*), and is obtained by the distillation of garlic with water. It occurs in many of the *Cruciferae*. It may be prepared artificially by digesting allyl iodide with potassium sulphide in alcoholic solution. It is a colorless, disagreeable-smelling oil, but slightly soluble in water. It boils at  $140^\circ$ . It affords crystalline precipitates with alcoholic solutions of  $HgCl_2$  and  $PtCl_4$ . With silver nitrate it yields the crystalline compound  $(C_3H_5)_2S.2AgNO_3$ .

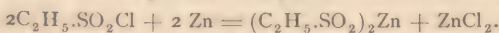
The sulphinic acids are nearly related to the sulphones:—



They contain the group  $-SO_2H$ , in which the H is linked to sulphur (see below), and in this instance it plays the rôle of acid hydrogen. Perhaps, too, these compounds might be considered derivatives of hyposulphurous acid,  $SO_2H_2$ . Their zinc salts are produced by the action of sulphur dioxide upon the zinc alkyls:—

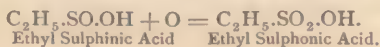


also from chlorides of the sulphonic acids by the action of zinc dust:—

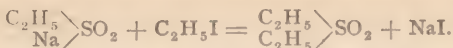


Barium hydrate will change the zinc salts into barium salts; these decomposed by sulphuric acid give the free sulphinic acids as thick, strongly acid liquids, which decompose on application of heat. Zinc ethyl sulphinate crystallizes in shining leaflets.

Oxidized by nitric acid the sulphinic acids readily become sulphonic acids (see p. 119).

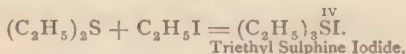


Sulphones result when the alkyl iodides act on the sodium salts of the sulphinic acids:—

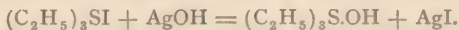


These facts demonstrate that in the sulphinic acids hydrogen is in union with sulphur (*Berichte*, 13, 1281).

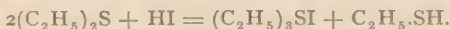
**Sulphine Compounds.** The sulphides of the alcohol radicals (thio-ethers) combine with the iodides (also with bromides and chlorides) of the alcohol radicals at ordinary temperatures, more rapidly on application of heat, and form crystalline compounds:—



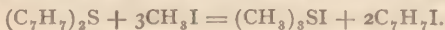
These are perfectly analogous to the halogen derivatives of the strong basic radicals (the alkali metals). By the action of moist silver oxide the halogen atom in them may be replaced by hydroxyl, and we get hydroxides similar to potassium hydroxide:—



The sulphine haloids are also obtained on heating the sulphur ethers with the halogen hydrides:—



The acid chlorides act similarly. Often when the alkyl iodides act on the sulphides of higher alkyls the latter are displaced (*Berichte*, 8, 325):—



$(\text{C}_2\text{H}_5)_2\text{S}.\text{CH}_3\text{I}$  and  $\text{C}_2\text{H}_5 \rangle \text{S}.\text{C}_2\text{H}_5\text{I}$  are to be isomeric (?), in which case a difference of the 4 valences of S would be proven (*Journ. pract. Chemie*, 14, 193).

The sulphine hydroxides are crystalline, efflorescent, strongly basic bodies, readily soluble in water. Like the alkalis they precipitate metallic hydroxides from metallic salts, set ammonia free from ammoniacal salts, absorb  $\text{CO}_2$  and saturate acids, with the formation of neutral salts:—



We thus observe that relations similar to those noted with nitrogen and phosphorus prevail with sulphur (also with selenium and tellurium). Nitrogen and phosphorus combine with four hydrogen atoms (also with alcoholic radicals) to form the groups ammonium,  $\text{NH}_4$ , and phosphonium,  $\text{PH}_4$ , which afford compounds similar to those of the alkali metals. Sulphur and its analogues combine in like manner with three monovalent alkyls, and give sulphonium and sulphine derivatives. Other metalloids and the less positive metals,

like lead and tin, exhibit a perfectly similar behavior. By addition of hydrogen or alkyls they acquire a strongly basic, metallic character (see the metallo-organic compounds).

Only the sulphine derivatives of methane and ethane have been carefully studied; the former are perfectly similar to the latter.

**Triethyl Sulphine Iodide**,  $(C_2H_5)_3SI$ , obtained by heating ethyl sulphide and iodide to  $100^\circ$ , crystallizes from water and alcohol in rhombic plates. Platinum chloride precipitates the double salt  $[(C_2H_5)_3SCI]_2.PtCl_4$ , from a solution of the chloride. It forms red needles.

**Triethyl Sulphine Hydroxide**,  $(C_2H_5)_3S.OH$ , forms efflorescent crystals and possesses an alkaline reaction. Its nitrate,  $(C_2H_5)_3S.O.NO_2$ , crystallizes in efflorescent scales. Hydrochloric acid converts the hydroxide into chloride,  $(C_2H_5)_3SCL$ .

### SELENIUM AND TELLURIUM COMPOUNDS.

These are perfectly analogous to the sulphur compounds. The methods of formation are also similar.

**Ethyl Hydroselenide**,  $C_2H_5.SeH$ , is a colorless, unpleasant-smelling, very mobile liquid. It combines readily with mercuric oxide to form a mercaptide.

**Ethyl Selenide**,  $(C_2H_5)_2Se$ , is a heavy, yellow oil, boiling at  $108^\circ$ . It unites directly with the halogens, *e. g.*,  $(C_2H_5)_2SeCl_2$ . It dissolves in nitric acid with formation of the oxide,  $(C_2H_5)_2SeO$ , which yields the salt,  $(C_2H_5)_2Se(NO_3)_2$ .

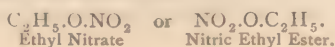
**Methyl Telluride**,  $(CH_3)_2Te$ , is obtained by distilling barium methyl sulphate with potassium telluride. It is a heavy, yellow oil, boiling from  $80-82^\circ$ . Dilute nitric acid converts it into the nitrate of the oxide,  $(CH_3)_2Te(NO_3)_2$ . From an aqueous solution of this salt hydrochloric acid precipitates a white, crystalline chloride,  $(CH_3)_2TeCl_2$ ; this yields the oxide,  $(CH_3)_2TeO$ , with silver oxide. This is a crystalline, efflorescent compound. In properties it resembles  $CaO$  and  $PbO$ . It reacts strongly alkaline, expels ammonia from ammonium salts, and forms salts by neutralizing acids.

Methyl telluride combines with methyl iodide to form **Trimethyl tellurium iodide**,  $(CH_3)_3TeI$ , which passes into the strongly basic hydroxide,  $(CH_3)_3Te.OH$ , by the action of moist silver oxide. It resembles potassium hydroxide.

**Ethyl Telluride**,  $(C_2H_5)_2Te$ , is a reddish-colored oil, soluble in nitric acid with formation of  $(C_2H_5)_2Te(NO_3)_2$ . Hydrochloric acid precipitates the chloride,  $(C_2H_5)_2TeCl_2$ , from an aqueous solution of the salt. Hydriodic acid precipitates the iodide,  $(C_2H_5)_2TeI_2$ . This is an orange-red powder, fusing at  $50^\circ$ .

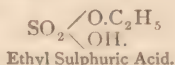
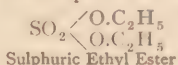
### ESTERS OF THE MINERAL ACIDS.

If we compare the alcohols with the metallic bases, the esters or compound ethers (see p. 105) are perfectly analogous in constitution to the salts. We can regard them as alcohol derivatives, arising by the substitution of acid radicals for alcoholic hydrogen, or they may be viewed as derivatives of the acids formed by substituting alcohol radicals for the hydrogen of acids. The various designations of esters would indicate this:—



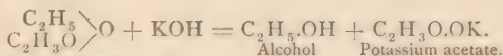


The first view is better adapted for esters of the polyhydric alcohols, while the second answers best for those of the polybasic acids. In these all or only one hydrogen can be replaced by alcohol radicals; thus arise the *neutral* esters and the so-called *ether-acids*, which correspond to the acid salts:—



Almost all the neutral esters are volatile; therefore the determination of their vapor density is a convenient means of establishing the molecular size and also the basicity of the acids. The ether-acids are not volatile, but soluble in water and yield salts with the bases.

All esters, and especially the ether-acids are decomposed into alcohols and acids when heated with water. Sodium and potassium hydrates, in aqueous or alkaline solution, accomplish this with great readiness when aided by heat. The process is termed *saponification*:—



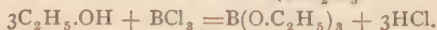
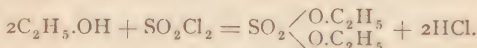
Ethyl acetate, ethyl acetic ester

There are two synthetic methods of producing the esters that favor the views of considering them derivatives of alcohols or acids. These are:—

(1) By reacting on the acids (their silver or alkali salts) with alkylogens:—



(2) By acting upon the alcohols or metallic alcoholates with acid chlorides:—



In addition to these reactions, which generally occur with ease, the esters can also be prepared by letting alcohols and acids act directly; water is also produced.



This transposition, however, only takes place gradually, progressing with time; it is accelerated by heat, but is never complete. We always find alcohols and acids together with the esters, and they do not react any further upon each other. If the *ester* be removed, *e. g.*, by distillation, from the mixture, as it is formed, an almost perfect reaction may be attained. These relations are perfectly similar to those observed in the action of two salts (compare Inorganic Chemistry). A more comprehensive statement of the processes taking place in the action of acids and alcohols will be given under the esters of the fatty acids.

When acted upon by alcohols, the polybasic acids mostly yield the primary esters or ether-acids. The haloid acids behave just like the mono-basic acids; the alkylogens formed (see p. 65) may be termed *haloid esters* of the alcohols.

## NITRIC ACID ETHERS (ESTERS).

**Methyl Nitrate**,  $\text{CH}_3.\text{O}.\text{NO}_2$ , *Nitric Methyl Ester*, is produced by distilling methyl alcohol with nitric acid. It is a colorless liquid, slightly soluble in water, and boiling at  $66^\circ$ . Its specific gravity, at  $20^\circ$ , is 1.182. When struck or heated to  $150^\circ$  it explodes very violently.

It is prepared by distilling a mixture of methyl alcohol (5 pts.) with sulphuric acid (10 pts.) and nitre (2 pts.), or a mixture of wood spirit and nitric acid, adding at the same time some urea (compare ethyl nitrate).

**Ethyl Nitrate**,  $\text{C}_2\text{H}_5.\text{O}.\text{NO}_2$ , *Nitric Ethyl Ester*. When alcohol is heated with nitric acid, there is a partial oxidation of the alcohol, which causes the formation of nitrous acid and nitrous ethyl ester. If, however, we destroy the nitrous acid (best by addition of urea), pure nitric ethyl ester results.

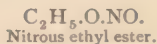
Distil 120–150 grms. of a mixture consisting of 1 volume nitric acid (of specific gravity 1.4) and 2 volumes alcohol (80–90 per cent.), to which 1–2 grams urea have been added. The distillate is shaken with water, and the heavier ester separated from the aqueous liquid.

Ethyl nitrate is a colorless, pleasant-smelling liquid, boiling at  $86^\circ$ , and having a specific gravity of 1.112, at  $15^\circ$ . It is almost insoluble in water, and burns with a white light. It will explode if suddenly exposed to high heat. Heated with ammonia it passes into ethylamine nitrate. Tin and hydrochloric acid convert it into hydroxylamine.

The propyl ester,  $\text{C}_3\text{H}_7.\text{O}.\text{NO}_2$ , (*Berichte* 14, 421) boils at  $110^\circ$ , the iso-propyl ester at  $101\text{--}102^\circ$ , and the isobutyl ester at  $123^\circ$ . Cetyl ester,  $\text{C}_{16}\text{H}_{33}.\text{O}.\text{NO}_2$ , solidifies at  $10^\circ$ .

## NITROUS ACID ETHERS (ESTERS).

These are isomeric with the nitro-paraffins (p. 79). The group  $\text{NO}_2$  is present in both; while, however, in the nitro-compounds nitrogen is combined with carbon, in the esters the union is effected by oxygen:—



The nitrous esters, as might be inferred from their different structure, decompose into alcohols and nitrous acid when acted on by alkalis. Similar treatment will not decompose the nitro-compounds. Nascent hydrogen (tin and hydrochloric acid) converts the latter into amines, while the esters yield alcohols.

Nitrous acid esters are produced in the action of nitrous acid upon the alcohols. The latter are saturated with nitrous acid vapors and distilled; or a mixture of alcohol,  $\text{KNO}_3$  and  $\text{H}_2\text{SO}_4$  is distilled.

**Methyl Nitrite**, Nitrous Methyl Ester,  $\text{CH}_3\cdot\text{O}\cdot\text{NO}$ , is an agreeable-smelling gas, that, by great cold, is condensed to a yellowish liquid, boiling at  $-12^\circ$ .

**Ethyl Nitrite**, Nitrous Ethyl Ester,  $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{NO}$ , is a mobile, yellowish liquid, of specific gravity 0.947, at  $15^\circ$ , and boils at  $+16^\circ$ . In water it is insoluble, and possesses an odor resembling that of apples. It is best obtained by heating a mixture of alcohol and nitric acid with copper turnings, or may be made by distilling a mixture of alcohol and fuming nitric acid, after having stood for some hours. The distillate is shaken with water (to withdraw alcohol) and a soda solution, then dehydrated and distilled (see *Annalen* 126, 71).

When ethyl nitrite stands with water it gradually decomposes, nitrogen oxide being eliminated; an explosion may occur under some conditions. Hydrogen sulphide changes it into alcohol and ammonia.

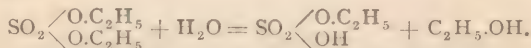
**Tertiary Butyl Nitrite**,  $\text{C}(\text{CH}_3)_3\cdot\text{O}\cdot\text{NO}$ , boils at  $77^\circ$ .

**Amyl Nitrite**,  $\text{C}_5\text{H}_{11}\cdot\text{O}\cdot\text{NO}$ , obtained by the distillation of fermentation amyl alcohol with nitric acid, is a yellow liquid, boiling at  $96^\circ$ . An explosion takes place when the vapors are heated to  $250^\circ$ . Nascent hydrogen changes it into amyl alcohol and ammonia. Heated with methyl alcohol it is transformed into methyl nitrite and amyl alcohol.

#### ESTERS OF SULPHURIC ACID (ETHYL SULPHATES).

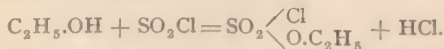
Sulphuric acid being dibasic forms two series of esters—the neutral esters and the primary esters or ether-acids (ethereal salts), (see p. 114).

(1) The *neutral esters* are formed by the action of the alkyl iodides upon silver sulphate,  $\text{SO}_4\text{Ag}_2$ ; they are also produced, in slight quantity on heating the primary esters, or alcohols with sulphuric acid. They can be extracted with chloroform from the product, and are heavy liquids, soluble in ether, possess an odor like that of peppermint, and boil without decomposition. They will sink in water, and gradually decompose into a primary ester and alcohol:—



The *Dimethyl Ester*,  $\text{SO}_2(\text{O}\cdot\text{CH}_3)_2$ —normal methyl sulphate—boils, without decomposition, at  $188^\circ$ . The *diethyl-ester*,  $\text{SO}_2(\text{O}\cdot\text{C}_2\text{H}_5)_2$ , normal ethyl sulphate, boils at  $208^\circ$ , sustaining at the same time a partial decomposition. When heated with alcohol, ethyl sulphuric acid and ethyl ether are formed (*Berichte* 13, 1699, 15, 947).

If sulphuryl chloride be permitted to act upon the alcohols esters of chlorsulphonic acid result:—



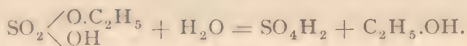
These are converted into ether-acids and alkyl chlorides when heated with more alcohol. They are strongly-smelling liquids, boiling without decomposition (ethyl chlorsulphonate  $\text{Cl}\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_2\text{H}_5$  boils at about  $150^\circ$ ), and are broken up into their components by water.

(2) The primary esters or ether-acids arise when the alcohols are mixed with concentrated sulphuric acid:—



The reaction takes place only when aided by heat, and it is not complete, because the mixture always contains free sulphuric acid and alcohol (compare p. 114). To isolate the ether-acids, the product of the reaction is diluted with water and boiled up with an excess of barium carbonate. In this way the unaffected sulphuric acid is thrown out as barium sulphate; the barium salts of the ether-acids are soluble and crystallize out when the solution is evaporated. To obtain the acids in a free state their salts are treated with sulphuric acid or the lead salts (obtained by saturating the acids with lead carbonate) may be decomposed by hydrogen sulphide, and the solution allowed to evaporate over sulphuric acid.

These acids are also prepared by the union of the alkylens with concentrated sulphuric acid (p. 54). They are thick liquids, that cannot be distilled. They sometimes crystallize. In water and alcohol they dissolve readily, but are insoluble in ether. When boiled or warmed with water they break up into sulphuric acid and water:—



When distilled they yield sulphuric acid and alkylens (p. 54); when heated with alcohols the products are simple and mixed ethers (p. 105).

They show a strongly acid reaction and furnish salts readily soluble in water, which are also mostly crystallized without great trouble. The salts gradually change to sulphates and alcohol when they are boiled with water. Those with the alkalies are frequently applied in different reactions. Thus with KSH and  $\text{K}_2\text{S}$  they yield mercaptans and thio-ethers (p. 108); with salts of fatty acids they furnish esters, and with KCN the alkyl cyanides, etc.

*Methyl Sulphuric Acid*,  $\text{SO}_4(\text{CH}_3)\text{H}$ , is a thick oil, that does not solidify at  $-30^\circ$ . The potassium salt,  $(\text{SO}_4)\text{CH}_3\text{K} + \frac{1}{2}\text{H}_2\text{O}$ , forms deliquescent leaflets.

The barium salt,  $(\text{CH}_3\cdot\text{SO}_4)_2\text{Ba} + 2\text{H}_2\text{O}$ , crystallizes in plates.

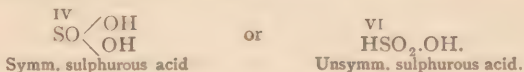
*Ethyl Sulphuric Acid*,  $\text{SO}_4(\text{C}_2\text{H}_5)\text{H}$ , is obtained by mixing 1 part alcohol with 2 parts concentrated sulphuric acid, and by the union of  $\text{C}_2\text{H}_4$  with sulphuric acid (p. 55). It is a thick, non-crystallizable liquid, having, at  $16^\circ$ , a specific gravity of 1.316. The potassium salt,  $\text{SO}_4(\text{C}_2\text{H}_5)\text{K}$ , is anhydrous and forms readily soluble tables. The barium and calcium salts crystallize in large tablets with two molecules of  $\text{H}_2\text{O}$  each. Consult *Annalen* 218, 299, for two different barium salts of methyl and ethyl sulphuric acid.

*Amyl Sulphuric Acid*,  $\text{SO}_4\cdot\text{C}_5\text{H}_{11}\text{H}$ . Two isomeric barium amyl sulphates are obtained by mixing ordinary fermentation amyl alcohol with sulphuric acid, and then neutralizing with barium carbonate. These salts both crystallize in large tablets, but show varying solubility in water, and may be separated by repeated crystallization. The more difficultly soluble salt is produced in the greater abundance and furnishes isobutyl carbinol, while active amyl alcohol is obtained from the more readily soluble salt (p. 100).

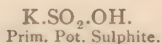
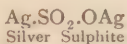


## SULPHUROUS ACID ETHERS (ESTERS).

The empirical formula of sulphurous acid,  $\text{SO}_3\text{H}_2$ , may have one of two possible structures:—



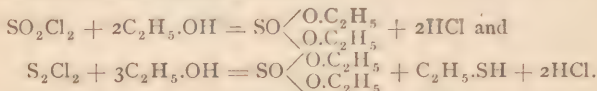
The ordinary sulphites correspond to formula 2, and it appears that in them one atom of metal is in direct combination with sulphur:—



This is evident from the following considerations:—

(1) *Esters of Symmetrical Sulphurous Acid.*

These arise in the action of thionyl chloride,  $\text{SOCl}_2$ , or sulphur mono-chloride,  $\text{S}_2\text{Cl}_2$ , upon alcohol:—

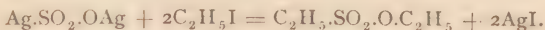


The mercaptan that is simultaneously formed sustains further decomposition. The sulphites thus produced are volatile liquids, insoluble in water, with an odor resembling that of peppermint, and decomposed by water, especially when heated, into alcohols and sulphurous acid.

**Sulphurous Methyl Ester**,  $\text{SO}(\text{O} \cdot \text{CH}_3)_2$ , methyl sulphite, boils at  $121^\circ$ .

The **Ethyl Ester**,  $\text{SO}(\text{O} \cdot \text{C}_2\text{H}_5)_2$ , boils at  $161^\circ$ . Its specific gravity at  $0^\circ$  is 1.106.  $\text{PCl}_3$  converts it into the chloride,  $\text{SO} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{O} \cdot \text{C}_2\text{H}_5 \end{array}$ , a liquid boiling at  $122^\circ$ , and decomposed by  $\text{H}_2\text{O}$  into alcohol,  $\text{SO}_2$  and  $\text{HCl}$ . It is isomeric with ethyl sulphonic chloride,  $\text{C}_2\text{H}_5 \cdot \text{SO}_2\text{Cl}$  (p. 120). On mixing the ester with a dilute solution of the equivalent amount of  $\text{KOH}$ , a potassium salt,  $\text{SO} \begin{array}{l} \diagup \text{O} \cdot \text{C}_2\text{H}_5 \\ \diagdown \text{OK} \end{array}$ , separates in glistening scales. This is viewed as a salt of the unstable ethyl sulphurous acid.

(2) *Esters of the Unsymmetrical Sulphurous Acid.*—These are formed by the action of silver sulphite upon the alkyl iodides in ethereal solution:—

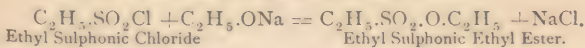


One of the alkyl groups is joined to sulphur, the other to oxygen. When heated with water the latter one only is separated as alcohol, and sulphonic acids result:—



Conversely, the esters can be prepared from the sulphonic acids,

by acting on their salts with alkyl iodides or upon the sodium alcohols with the chlorides of the sulphonic acids:—



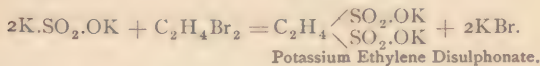
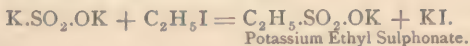
Hence, the esters formed from silver sulphite may be regarded as esters of the sulpho-acids. They boil much higher than the isomeric esters of symmetrical sulphurous acid. They are distinguished from the latter by having but one of their alkyl groups separated out by alkalis (see above).

**Ethyl Sulphonic Ethyl Ester**,  $\text{C}_2\text{H}_5\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , produced as above described, boils at  $213.4^\circ$ , and has a sp. gr. of 1.171 at  $0^\circ$ .

The methyl ester,  $\text{C}_2\text{H}_5\cdot\text{SO}_2\cdot\text{O}\cdot\text{CH}_3$ , boils at  $198^\circ$ .

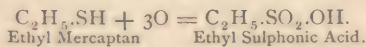
### 3. Sulpho-acids, $\text{C}_n\text{H}_{2n+1}\cdot\text{SO}_2\cdot\text{OH}$ .

The sulpho- or sulphonic acids, which contain the group  $-\text{SO}_2\cdot\text{OH}$  attached to carbon, may be viewed as esters of unsymmetrical sulphurous acid,  $\text{HSO}_2\text{OH}$ , inasmuch as they are produced from its neutral esters by the separation of an alkyl group (p. 118). Furthermore, their salts are directly obtained from the alkaline sulphites by heating them with alkylogens (in concentrated aqueous solution to  $120-150^\circ$ ):—



Just as sulphurous acid (its salts) unites with alkyl iodides to form alkyl sulphonic acids, so can other unsaturated mineral acids (nitrous and arsenious acid) give rise to derivatives of analogous constitution (compare the nitro-paraffins and methyl arsenic acid). The usual explanation of this is found in the unsymmetrical constitution of these acids; it may, perhaps, depend on the fact, that the lower acids are also unsaturated (*Berichte*, 16, 1439).

The oxidation of mercaptans and alkyl disulphides (p. 110) (also sulphocyanides) with nitric acid also affords the sulpho-acids:



Therefore, these sulpho-acids can be again reduced to mercaptans (by action of zinc and hydrochloric acid upon their chlorides—as  $\text{C}_2\text{H}_5\cdot\text{SO}_2\text{Cl}$ ):  $\text{C}_2\text{H}_5\cdot\text{SO}_2\text{Cl} + 3\text{H}_2 = \text{C}_2\text{H}_5\cdot\text{SH} + \text{HCl} + 2\text{H}_2\text{O}$ . They may also be obtained by oxidizing the sulphinic acids and can be again converted into the latter (see p. 111). All these reactions plainly indicate that in the sulpho-acids the alkyl group is joined to sulphur, and that, therefore, it is very probable that in the sulphites the one atom of metal is directly combined with sulphur. Finally, the sulpho-acids can be prepared by the action of sulphuric acid or sulphur trioxide ( $\text{SO}_3$ ) upon alcohols, ethers and

various other bodies. This reaction is very general and easily executed with the benzene derivatives.

These acids are thick liquids, readily soluble in water, and, as a usual thing, generally crystallizable. They suffer decomposition when exposed to heat but are not altered when boiled with alkaline hydrates. When fused with solid alkalies they break up into *sulphites* and alcohols:—



$\text{PCl}_5$  changes them to chlorides, *e. g.*,  $\text{C}_2\text{H}_5\cdot\text{SO}_2\text{Cl}$ , which become mercaptans through the agency of hydrogen, or by the action of sodium alcoholates pass into the neutral esters— $\text{C}_2\text{H}_5\cdot\text{SO}_3\cdot\text{C}_2\text{H}_5$  (p. 118).

**Methyl Sulphonic Acid**,  $\text{CH}_3\cdot\text{SO}_3\text{H}$ , is a thick, uncrystallizable liquid, soluble in water. When heated above  $130^\circ$  it sustains decomposition. In order to obtain the pure acid it is converted into the lead salt, the solution of which is treated with  $\text{H}_2\text{S}$ , the lead sulphide filtered off and the filtrate concentrated.

Its salts are readily soluble in water and crystallize well. The barium salt,  $(\text{CH}_3\cdot\text{SO}_3)_2\text{Ba} + 1\frac{1}{2}\text{H}_2\text{O}$ , crystallizes in rhombic plates. Methyl sulphonic chloride,  $\text{CH}_3\cdot\text{SO}_2\text{Cl}$ , boils near  $160^\circ$  and is slowly decomposed by water into the acid and hydrogen chloride.

The following is an interesting method of preparing methyl sulphonic acid. Moist chlorine is allowed to act upon carbon disulphide,  $\text{CS}_2$ , when there is produced the compound,  $\text{CCl}_3\cdot\text{SO}_2$ , which we must consider as the chloride of trichlormethyl sulphonic acid,  $\text{CCl}_3\cdot\text{SO}_2\text{Cl}$ . This is a colorless, crystalline body fusing at  $135^\circ$ , and boiling at  $170^\circ$ . It is soluble in alcohol and ether, but not in water. Its odor resembles that of camphor and excites tears. To prepare the chloride a mixture of 500 gr.  $\text{HCl}$ , 300 grms. coarse grained  $\text{Cr}_2\text{O}_3\cdot\text{K}_2$ , 200 gr. nitric acid and 30 gr.  $\text{CS}_2$ , are allowed to stand in an open flask. Water is then added, to dissolve the salts, and the crystals of  $\text{CCl}_3\cdot\text{SO}_2$  are filtered off.

On boiling the chloride with potassium or barium hydrate salts of trichlormethyl sulphonic acid,  $\text{CCl}_3\cdot\text{SO}_3\text{H}$ , are formed. The barium salt,  $(\text{CCl}_3\cdot\text{SO}_3)_2\text{Ba} - \text{H}_2\text{O}$ , crystallizes in leaflets. Sulphuric acid releases the acid from it. It consists of deliquescent prisms. Nascent hydrogen (sodium amalgam) in an aqueous solution of the acid produces successively  $\text{CHCl}_2\cdot\text{SO}_3\text{H}$ ,  $\text{CH}_2\text{Cl}\cdot\text{SO}_3\text{H}$ , and finally  $\text{CH}_3\cdot\text{SO}_3\text{H}$ —methyl sulphonic acid. These reactions represent one of the first instances of the conversion of an inorganic (mineral) substance ( $\text{CS}_2$ ) into a so-called organic derivative.

**Ethyl Sulphonic Acid**,  $\text{C}_2\text{H}_5\cdot\text{SO}_3\text{H}$ , is a thick, crystallizable liquid. Its lead salt,  $(\text{C}_2\text{H}_5\cdot\text{SO}_3)_2\text{Pb}$ , crystallizes in readily soluble leaflets. Nitric acid oxidizes it to ethyl sulphuric acid,  $\text{SO}_4(\text{C}_2\text{H}_5)_2\text{H}$ . Its chloride,  $\text{C}_2\text{H}_5\cdot\text{SO}_2\text{Cl}$ , is a liquid, boiling at  $173^\circ$ .

## ESTERS OF THIO-SULPHURIC ACID.

On p. 119 we saw how the alkyl sulphonic acids were obtained from the sulphites by the alkyl iodides. In the same way the corresponding *alkyl thiosulphonic acids* can be prepared from the salts of thiosulphuric acid (hyposulphurous acid):—



Only the primary saturated alkyl iodides, however, react in this way (*Berichte*, 15, 1939). The ethyl compound can be made, too, by letting iodine act on a mixture of mercaptan and sodium sulphite,  $\text{Na}_2\text{SO}_3$ .

The salts of these acids crystallize well. When boiled with hydrochloric acid they are decomposed into mercaptans and sulphurous acid. When heated they break up into alkyl disulphides,  $(\text{C}_2\text{H}_5)_2\text{S}_2$ , and dithionates  $(\text{SO}_4\text{K}_2 + \text{SO}_2)$ .

## ESTERS OF PERCHLORIC ACID.

**Ethyl Perchlorate**,  $\text{C}_2\text{H}_5\text{.ClO}_4$ , is obtained by the action of ethyl iodide upon silver perchlorate. A colorless liquid that explodes when heated.

## ESTERS OF BORIC ACID.

The esters of the tribasic acid,  $\text{B(OH)}_3$ , are formed along with those of the monobasic acid,  $\text{BO.OH}$ , when  $\text{BCl}_3$  acts upon the alcohols. The first are volatile, thick liquids, while the second decompose when distilled. Acid esters are not known. Water decomposes both the preceding varieties.

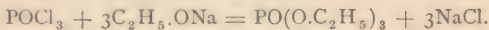
**Methyl Borate**,  $\text{B(O.CH}_3)_3$ , boils at  $65^\circ$ .

**Ethyl Borate**,  $\text{B(O.C}_2\text{H}_5)_3$ , is obtained by distilling potassium ethyl sulphate together with borax. It boils at  $119^\circ$ .

## ESTERS OF THE PHOSPHORIC ACIDS.

Tribasic phosphoric acid,  $\text{PO(OH)}_3$ , yields three series of esters—the primary, secondary and tertiary, all of which are thick liquids. Only the last volatilize without decomposition.

**Phosphoric Triethyl Ester**,  $\text{PO(O.C}_2\text{H}_5)_3$ , is formed when phosphorus oxychloride acts upon sodium ethylate:—



A thick liquid, soluble in water, alcohol and ether, and boiling at  $215^\circ$ . The aqueous solution decomposes readily into diethyl-phosphoric acid, the lead salt of which is made by boiling with  $\text{PbO}$ .

**Diethyl Phosphoric Acid**,  $\text{PO} \left\{ \begin{smallmatrix} (\text{O.C}_2\text{H}_5)_2 \\ \text{OH} \end{smallmatrix} \right.$ . Obtained by decomposing the lead salt with  $\text{H}_2\text{S}$ . It is a thick syrup. The lead salt crystallizes in silky needles. When heated it passes into the triethyl ester and lead monoethyl phosphate, insoluble in water. The acid of this last salt has the formula  $\text{PO(OH)}_2\text{.O.C}_2\text{H}_5$ .

The esters of symmetrical phosphorous acid,  $\text{P(OH)}_3$ , result when  $\text{PCl}_3$  acts on the alcohols. Triethyl phosphite,  $\text{P(O.C}_2\text{H}_5)_3$ , boils at  $191^\circ$ .

Acids of the structure  $\text{C}_2\text{H}_5\text{.PO(OH)}_2$ , corresponding to the sulpho-acids,  $\text{C}_2\text{H}_5\text{.SO}_3\text{.OH}$ , (p. 119) may be derived from the unsymmetrical phosphorous acid,  $\text{HPO(OH)}_2$ . They are produced by the oxidation of primary phosphines (see these) with nitric acid:—



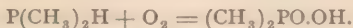


They are spermaceti-like, crystalline bodies, soluble in water and reacting strongly acid. They furnish both acid and neutral salts, that are mostly crystallizable.

**Methyl Phosphite**,  $\text{CH}_3\text{PO}(\text{OH})_2$ , melts at  $105^\circ$ .  $\text{PCl}_5$  converts it into  $\text{CH}_3\cdot\text{POCl}_2$ , which fuses at  $32^\circ$ , and boils at  $163^\circ$ . Water again produces the acid from the chloride.

**Ethyl Phosphite**,  $\text{C}_2\text{H}_5\cdot\text{PO}(\text{OH})_2$ , melts at  $44^\circ$ .

From hypophosphorous acid,  $\text{H}_2\cdot\text{PO}\cdot\text{OH}$ , we obtain similar compounds that can be called *phosphinic acids*. They result when nitric acid acts on the secondary phosphines:—



**Dimethyl Phosphinic Acid**,  $(\text{CH}_3)_2\text{PO}\cdot\text{OH}$ , resembles paraffin, fuses at  $76^\circ$  and volatilizes without decomposition.

### ESTERS OF ARSENIC ACIDS.

**Ethyl Arsenate**,  $\text{AsO}(\text{O}\cdot\text{C}_2\text{H}_5)_3$ , is the product of the action of ethyl iodide upon silver arsenate,  $\text{AsO}_4\text{Ag}_3$ . It is a liquid, boiling at  $235^\circ$ .

The Esters of arsenious acid,  $\text{As}(\text{OH})_3$ , form when  $\text{AsBr}_3$  is distilled with sodium alcoholates. They distil without decomposition. Water immediately changes them to arsenious acid and alcohols. The methyl ester,  $\text{As}(\text{O}\cdot\text{CH}_3)_3$ , boils at  $128^\circ$ ; the ethyl ester at  $166^\circ$ .

Arsenic compounds analogous to the phosphorous and phosphinic acids,  $(\text{C}_2\text{H}_5)_2\text{PO}(\text{OH})_2$  and  $(\text{C}_2\text{H}_5)_2\text{PO}\cdot\text{OH}$ , exist. They are: methyl arsenic acid,  $\text{CH}_3\cdot\text{AsO}(\text{OH})_2$ , and dimethyl arsenic acid,  $(\text{CH}_3)_2\text{AsO}\cdot\text{OH}$ , or *cacodylic acid*. These will be considered with arsenic alcoholic radicals.

### ESTERS OF SILICIC ACID.

These are obtained by the action of  $\text{SiCl}_4$  and  $\text{SiFl}_4$  upon alcohols or sodium alcoholates. The esters of normal silicic acid,  $\text{Si}(\text{OH})_4$ , of metasilicic acid,  $\text{SiO}(\text{OH})_2$ , and disilicic acid,  $\text{Si}_2\text{O}_7\text{H}_2$ , are formed together and can be separated by fractional distillation.

The normal *Methyl Ester*,  $\text{Si}(\text{O}\cdot\text{CH}_3)_4$ , boils at  $120\text{--}122^\circ$ ; methyl disilicate,  $\text{Si}_2\text{O}_7(\text{CH}_3)_6$ , at  $202^\circ$ .

The *Ethyl Ester*,  $\text{Si}(\text{O}\cdot\text{C}_2\text{H}_5)_4$ , boils at  $165^\circ$ . Ethyl disilicate,  $\text{Si}_2\text{O}_7(\text{C}_2\text{H}_5)_6$ , which can also be produced by action of silicon oxychloride,  $\text{Si}_2\text{OCl}_6$ , on alcohol, boils at  $236^\circ$ ; ethyl-metasilicate,  $\text{SiO}(\text{O}\cdot\text{C}_2\text{H}_5)_2$ , boils at  $360^\circ$ .

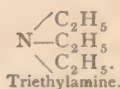
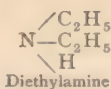
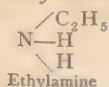
These derivatives on standing awhile in moist air, or by addition of water, slowly decompose with separation of silicic acid, which sometimes solidifies to a transparent hard glass.

### AMINES.

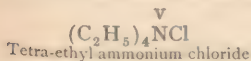
Among the derivatives of carbon exists a series of strong basic bodies, which have been designated organic bases or alkaloids. They all contain nitrogen and are viewed as ammonia derivatives; this accounts for their basic character. We will consider here only the *monamines* derived from ammonia by the replacement of hydrogen by monovalent alkyls.

One, two and three hydrogen atoms of the ammonia molecule

may suffer this replacement, thus affording the *primary*, *secondary* and *tertiary amines* :—

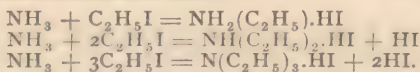


Derivatives also exist that correspond to the ammonium salts and hypothetical ammonium hydroxide,  $\text{NH}_4.\text{OH}$  :—



The following methods are the most important for preparing the above compounds :—

(1) The iodides or bromides of the alcohol radicals are heated to  $100^\circ$ , in sealed tubes, with alcoholic ammonia (*A. W. Hoffmann*, 1849). In this way the alkyl displaces the hydrogen of ammonia; the hydrogen haloid formed at the same time combines with the amine and yields ammonium salts :—



When these salts are distilled with sodium or potassium hydroxide, free amines pass over :—

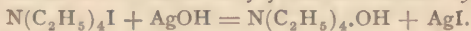


It is interesting to know that the primary alkyl iodides form both secondary and tertiary amines, while the secondary alkyl iodides (like isopropyl iodide) only furnish primary amines (also alkylens) (*Berichte* 15, 1288).

In the same process tertiary amines further unite with alkyl iodides and form tetra-alkyl ammonium salts :—

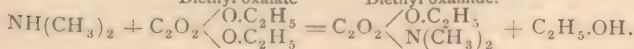
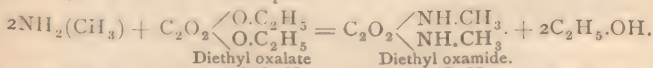


These are *not* decomposed when distilled with  $\text{KOH}$ ; but if treated with moist silver oxide they yield *ammonium hydroxides* :—

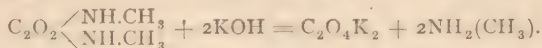


By the action of primary alkylgens upon ammonia, a mixture of primary, secondary and tertiary amine salts and those of the ammonium bases, always results. The latter may be easily obtained pure by distilling the mixture with  $\text{KOH}$ , when the amines pass over and the ammonium bases make up the residue, inasmuch as their halogen compounds are not decomposed by alkalies.

Fractional distillation is a poor means of separating the amines. The following procedure serves this purpose better (*Berichte* 8, 760): The mixture of the dry bases is treated with diethyl oxalate, when the primary amine, *e. g.*, methylamine, is changed to diethyl oxamide, which is soluble in water; dimethylamine is converted into the ester of dimethyl oxamic acid (see oxalic acid compounds); and trimethylamine is not acted upon :—



When the reaction-product is distilled the unaltered trimethylamine passes over. Water will extract the dimethyl oxamide from the residue; on distillation with caustic potash it becomes *methylamine* and potassium oxalate:—



The insoluble dimethyl-oxamic ester is converted, by distillation with potash into *dimethylamine*:—



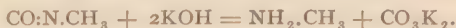
Another procedure furnishing a partial separation of the amines depends on their varying behavior towards carbon disulphide. The free bases (in aqueous, alcoholic or ethereal solution) are digested with  $\text{CS}_2$ , when the primary and secondary amines form salts of the alkyl dithio-carbaminic acids (see these), while the tertiary amines remain unaffected, and may be distilled off. On boiling the residue with  $\text{HgCl}_2$  or  $\text{FeCl}_3$ , a part of the primary amine is expelled from the compound as mustard oil (*Berichte*, 14, 2754 and 15, 1290).

The esters of nitric acid, when heated to  $100^\circ$  with alcoholic ammonia, react in a manner analogous to the alkyl iodides:—

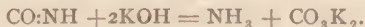


This reaction is often very convenient for the preparation of the primary amines (*Berichte* 14, 421).

(2) The ethers of isocyanic or isocyanuric acid are distilled with potassium hydrate (*Würtz*, 1848):—



Cyanic acid affords ammonia in precisely the same manner:—

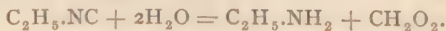


In the above reaction only primary amines are produced.

To convert alcoholic radicals into corresponding amines, the iodides are heated together with silver cyanate; the product of the reaction is then mixed with pulverized caustic soda, and distilled in an oil bath (*Berichte* 10, 131).

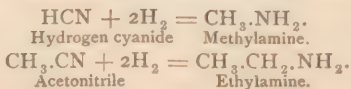
Above we observed the decomposition of the isocyanic ethers by alkalis. Their analogues in constitution—the isothio-cyanic ethers (the mustard oils, etc.)—are also broken up into primary amines by sulphuric acid.

3. Warm the isocyanides of the alkyls with dilute hydrochloric acid; formic acid will split off (*A. W. Hoffmann*):—

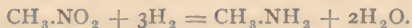


The isocyanides are obtained by heating the alkyl iodides with silver cyanide (see this).

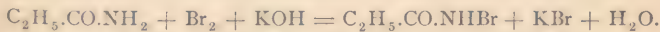
(4) By the action of nascent hydrogen upon the nitrites or alkyl cyanides (*Mendius*):—



(5) By action of nascent hydrogen (HCl and Zn) upon the nitro-paraffins (p. 78):—



(6) A method entirely new, and especially adapted to the formation of primary amines, consists in the transformation of fatty acids (*A. W. Hoffmann, Berichte* **14**, 762). The amides of these acids are converted, through the agency of Br and KOH, into brom-amides:—

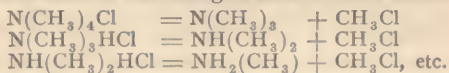


On further heating with alkali, carbon dioxide escapes and primary amines result:—



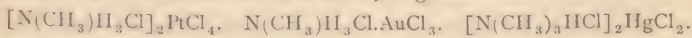
The methods above are the ordinary ones; others exist for the production of amines; *e. g.*, they arise in the decomposition of complex nitrogenous derivatives, as shown in the case of the amido-acids.

Tertiary, secondary and primary amines may also be obtained by the dry distillation of the halogen salts of the ammonium bases:—



These reactions serve for the commercial production of methyl chloride from trimethylamine.

The amines are very similar to ammonia in their deportment. The lower members are gases, with ammoniacal odor, and are very readily soluble in water; their combustibility distinguishes them from ammonia. The higher members are liquids, soluble in water, and only the highest are difficultly soluble. The amines are best dehydrated by distillation over barium oxide. Their basicity is greater than that of ammonia, and increases with the number of alkyls introduced; the tertiary amines are stronger bases than the secondary, and the latter stronger than the primary. Therefore, they can expel ammonia from the ammonium salts. Like ammonia, they unite directly with acids to form salts, which differ from ammoniacal salts by their solubility in alcohol. They combine with some metallic chlorides, and afford compounds perfectly analogous to the ammonium double salts; *e. g.*:—

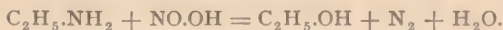


The ammonia in the alums, the cuprammonium salts and other compounds may be replaced by amines.

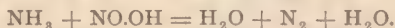
The behavior of amines with nitrous acid is very characteristic. The latter compound converts the primary amines (better to act on



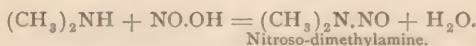
the haloid salts with  $\text{AgNO}_2$ ) into the corresponding alcohols (see p. 91):—



This is a reaction analogous in every respect to the decomposition of ammonium nitrite into water and nitrogen:—



Nitrous acid changes the secondary amines to nitroso-amines (p. 128):—



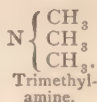
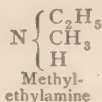
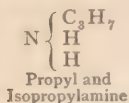
The tertiary amines remain intact or suffer decomposition.

When aided by heat  $\text{KMnO}_4$  breaks up the amines, nitrogen being eliminated and the alkyls being oxidized to aldehydes and acids (*Ber.*, 8, 1237).

Bromine in alkaline solution converts the primary amines (their  $\text{HCl}$  salts) into alkylized nitrogen dibromides, *e. g.*,  $\text{C}_2\text{H}_5\cdot\text{NBr}_2$ , the secondary amines at the same time throw off alkyl bromides and become primary amines (*Ber.*, 16, 558):—



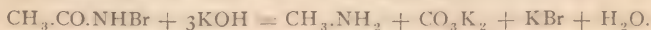
The possible isomerides of the amines are very numerous; they are determined not only by the isomerism of alcoholic radicals, but also by the number of replacing groups, as is manifest from the following examples:—



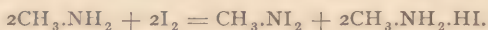
They are thus distinguished: by the action of ethyl iodide the primary amines can receive two, the secondary, however, only one additional ethyl group. The power of forming carbylamines and mustard oils (see these) is especially characteristic of the primary amines; these are easily recognized by the odor (*Ber.*, 8, 108 and 461).

#### PRIMARY AMINES.

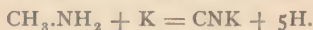
**Methylamine**,  $\text{CH}_3\cdot\text{NH}_2$ , is produced when the methyl ester of cyanic acid is heated with potash (p. 124); by the action of tin and hydrochloric acid upon chloropicrin,  $\text{CCl}_3(\text{NO}_2)$ ; when nascent hydrogen acts upon hydrogen cyanide; and by the decomposition of various natural alkaloids, like theine, creatine, and morphine. The best way of preparing it is to warm brom-acetamide with caustic potash (see p. 125 and *Ber.*, 14, 764):—



Methylamine is a colorless gas, with ammoniacal odor, and condenses to a liquid below  $0^{\circ}$ . Its combustibility in the air distinguishes it from ammonia. At  $12^{\circ}$  1 volume of water dissolves 1150 volumes of the gas. The aqueous solution manifests all the properties of aqueous ammonia, but does not, however, dissolve the oxides of cobalt, nickel and cadmium. Iodine (also Br) throws out a dark red precipitate,  $\text{CH}_3\cdot\text{NI}_2$ , from the solution:—



When methylamine is passed over heated potassium it decomposes into potassium cyanide and hydrogen:—



The salts of methylamine are soluble in water. Its hydrochloride crystallizes in large, deliquescent leaflets, fusing at  $100^{\circ}$  and distilling without decomposition. It affords a yellow, crystalline, double salt— $[\text{NH}_2(\text{CH}_3)\text{HCl}]_2\cdot\text{PtCl}_4$ —with  $\text{PtCl}_4$ .

**Ethylamine**,  $\text{C}_2\text{H}_5\cdot\text{NH}_2$ , is a mobile liquid, that boils at  $18^{\circ}$  and has a sp. gr. of 0.696 at  $8^{\circ}$ . It expels ammonia from ammoniacal salts, and when in excess redissolves aluminium hydrate; otherwise it deports itself in every respect like ammonia.

Its HCl salt,  $\text{NH}_3(\text{C}_2\text{H}_5)\text{Cl}$ , crystallizes in large, deliquescent leaflets, fusing at  $80^{\circ}$ . Its platinum double salt crystallizes in orange red rhombohedra. Like ammonia, it also combines with  $\text{PtCl}_2$  to form  $\text{PtCl}_2(\text{C}_2\text{H}_5\cdot\text{NH}_2)_2$ . It exists as a white mass when in union with  $\text{CO}_2$  and in this condition if added to a  $\text{BaCl}_2$  solution it gradually precipitates barium carbonate. It probably corresponds to ammonium carbamate.

**Propylamine**,  $\text{C}_3\text{H}_7\cdot\text{NH}_2$ , boils at  $49^{\circ}$ ; **isopropylamine**,  $\text{C}_3\text{H}_7\cdot\text{NH}_2$ , at  $31^{\circ}\text{--}32^{\circ}$ .

**Butylamine**,  $\text{C}_4\text{H}_9\cdot\text{NH}_2$  (normal), boils at  $76^{\circ}$ ; **isobutylamine**,  $\text{C}_4\text{H}_9\cdot\text{NH}_2$ , obtained from fermentation butyl alcohol and from ordinary valeramide, boils at  $66^{\circ}$ .

**Normal Amylamine**,  $\text{C}_5\text{H}_{11}\cdot\text{NH}_2$ , from normal caproylamide,  $\text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{NH}_2$ , boils at  $103^{\circ}$ .

**Isoamylamine**,  $\text{C}_5\text{H}_{11}\cdot\text{NH}_2$ , is a liquid boiling at  $95^{\circ}$ ; it is obtained from leucine by distillation with caustic potash or from isocaproylamide. It is miscible with water, and burns with a luminous flame. **Nonylamine**,  $\text{C}_9\text{H}_{19}\cdot\text{NH}_2$ , obtained from normal caprylamide, boils about  $195^{\circ}$ , and is difficultly soluble in water.

**Allylamine**,  $\text{C}_3\text{H}_5\cdot\text{NH}_2$ , is obtained by the action of concentrated sulphuric acid or zinc and hydrochloric acid upon mustard oil ( $\text{C}_3\text{H}_5\cdot\text{N}:\text{CS}$ ); it is a liquid boiling at  $58^{\circ}$ .

## SECONDARY AMINES.

**Dimethylamine**,  $\text{NH}(\text{CH}_3)_2$ , is a gas that dissolves readily in water, and that can be condensed to a liquid below  $+8^{\circ}$ . It is most conveniently obtained by boiling nitroso-dimethyl aniline or dinitro-dimethyl aniline with caustic potash (*Annalen*, 222, 119). The platinum double salt crystallizes in large needles.

**Diethylamine**,  $\text{NH}(\text{C}_2\text{H}_5)_2$ , is a liquid boiling at  $57^\circ$  and readily soluble in water. Its  $\text{HCl}$  salt fuses at  $216^\circ$  and boils at  $325^\circ$ .

The secondary amines are also designated imide-bases.

Sulphamides, *e. g.*,  $\text{SO}_2 \begin{smallmatrix} \diagup \text{N}(\text{CH}_3)_2 \\ \diagdown \text{N}(\text{CH}_3)_2 \end{smallmatrix}$ , are formed by the action of sulphuryl chloride,  $\text{SO}_2\text{Cl}_2$ , upon the free secondary amines, whereas when the  $\text{HCl}$  salts are employed their chlorides result,  $\text{SO}_2 \begin{smallmatrix} \diagup \text{NR}_2 \\ \diagdown \text{Cl} \end{smallmatrix}$ ; these are converted, through the agency of water, into sulphaminic acids,  $\text{SO}_2 \begin{smallmatrix} \diagup \text{NR}_2 \\ \diagdown \text{OH} \end{smallmatrix}$  (*Annalen*, 222, 118).

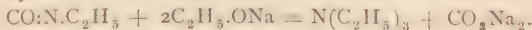
**Nitroso-amines.** These are compounds having the nitroso-group attached to  $\text{N}$  (p. 78). All basic secondary amines (imines) like  $(\text{CH}_3)_2\text{NH}$  and  $\text{C}_6\text{H}_5 \begin{smallmatrix} \diagup \text{NH} \\ \diagdown \text{C}_2\text{H}_3\text{O} \end{smallmatrix}$  can become nitroso-amines through the replacement of the hydrogen of the imide group. They are obtained from the free imides by the action of nitrous acid upon their aqueous, ethereal, or glacial acetic acid solutions, or by warming their salts in aqueous or acid solution with potassium nitrite (*Berichte*, 9, 112). They are mostly oily, yellow liquids, insoluble in water, and may be distilled without suffering decomposition. Alkalies and acids are usually without effect upon them; with phenol and sulphuric acid they give the nitroso reaction (see p. 79). When reduced in alcoholic solution by means of zinc dust and acetic acid they become hydrazines (p. 129).

**Dimethyl Nitrosamine**,  $(\text{CH}_3)_2\text{N.NO}$ , is a yellow oil, of penetrating odor. **Diethyl Nitrosamine**,  $(\text{C}_2\text{H}_5)_2\text{N.NO}$ , is also an oil, boiling at  $177^\circ$ ; it is obtained from  $\text{HCl}$ -diethylamine by distilling it with  $\text{KNO}_2$  in aqueous solution. Concentrated hydrochloric acid regenerates diethylamine from it.

### TERTIARY AMINES.

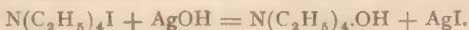
**Trimethylamine**,  $\text{N}(\text{CH}_3)_3$ . This is isomeric with propylamine,  $\text{C}_3\text{H}_7\text{NH}_2$ , and is present in herring-brine; it is produced by distilling betaine (from the beet) with caustic potash. It is prepared from herring-brine in large quantities, and also by the distillation of the "vinasses" of the French beet root. Trimethylamine is a liquid, very soluble in water, and boils at  $9.3^\circ$ . The penetrating, fish-like smell is characteristic of it. The  $\text{HCl}$ -salt is very deliquescent.

**Triethylamine**,  $\text{N}(\text{C}_2\text{H}_5)_3$ , boils at  $89^\circ$  and is not very soluble in water. It is also produced by heating ethyl isocyanate with sodium ethylate:—



### AMMONIUM BASES.

The tertiary amines combine with alkyl iodides and yield ammonium iodides; these are scarcely affected by the alkalies, even on boiling (p. 123); but when treated with moist silver oxide the *ammonium hydroxides* are formed:—



These hydroxides are perfectly analogous to those of potassium and sodium. They possess strong alkaline reaction, saponify fats, and deliquesce in the air. They crystallize when their aqueous solution is concentrated in vacuo. With the acids they yield ammonium salts, that, for the most part, crystallize well.

When they are exposed to strong heat they break up into tertiary amines and alcohols or their decomposition products ( $C_nH_{2n}$  and  $H_2O$ ):—



If the ammonium base should contain different alkyls, those higher in structure split off (*Berichte*, 14, 494).

If iodine is added to the aqueous solution of the iodides, we have compounds precipitated which contain three and five atoms of iodine:  $(C_2H_5)_4NI.I_2$  and  $(C_2H_5)_4NI.2I_2$ .

The tri-iodides are mostly dark violet bodies; the penta-iodides resemble iodine very much.

**Tetraethyl Ammonium Iodide**,  $N(C_2H_5)_4I$ , is obtained by mixing triethylamine with ethyl iodide; the mixture becomes warm and when it cools is crystalline. It separates from water or alcohol in large prisms, that fuse when heated and then decompose into  $N(C_2H_5)_3$  and  $C_2H_5I$ . Moist silver oxide converts it into

**Tetraethyl Ammonium Hydroxide**,  $N(C_2H_5)_4OH$ , which crystallizes in delicate, deliquescent needles. It absorbs  $CO_2$  from the air with avidity. Its platinum double salt,  $[N(C_2H_5)_4Cl]_2.PtCl_4$ , crystallizes in octahedrons.

**Tetraethyl Ammonium Cyanide**,  $(C_2H_5)_4N.CN$ , is a white, crystalline mass. It is obtained by acting on the hydroxide with  $HCN$ , or upon the iodide with barium cyanide. When boiled with alkalis it decomposes into  $NI_3$ , formic acid and ammonium hydroxide.

**Dimethyl-diethyl Ammonium Chloride**,  $\left\{ \begin{smallmatrix} (CH_3)_2 \\ (C_2H_5)_2 \end{smallmatrix} \right\} NCl$ , is obtained from dimethylamine and ethyl iodide and also from diethylamine and methyl iodide:



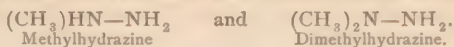
These two are identical (*Annalen*, 180, 273). They demonstrate, too, that the ammonium compounds are not molecular derivatives as formerly assumed (the above formulas are only intended to exhibit the different manner of formation), but represent true atomic compounds. The equivalence of the five nitrogen valences is also thus proven.

## HYDRAZINES.

Just as the *amines* are derived from ammonia,  $NH_3$ , so the *hydrazines* are derived from *hydrazine* or *diamide*,  $H_2N-NH_2$ . This is not known, but analogues of it are liquid hydrogen phosphide,  $H_2P-PH_2$ , and dimethylarsine (cacodyl),  $(CH_3)_2As-As(CH_3)_2$ .



The only derivatives of hydrazine as yet known are those with one or two alkyls (alcohol radicals) (see Phenylhydrazine), like—



These are prepared by acting upon the aqueous or alcoholic solution of the nitroso-amines with zinc dust and acetic acid:—



Nitroso-amines containing acid radicals, *e. g.*,  $\text{C}_6\text{H}_5\text{N.NO}$ ,  $\text{C}_2\text{H}_3\text{O}$ , do not give corresponding hydrazines, but the amides, on reduction.

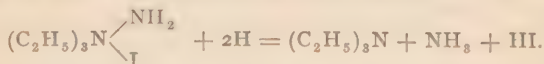
As respects physical and chemical properties the hydrazines closely resemble the amines; they are distinguished from them by their ability to reduce alkaline copper solutions. The hydrazines are powerful bases, uniting with one and two equivalents of acids to form salts.

**Dimethyl Hydrazine**,  $(\text{CH}_3)_2\text{N.NH}_2$ , and **Diethyl Hydrazine**,  $(\text{C}_2\text{H}_5)_2\text{N.NH}_2$ , are easily volatilized liquids, of ammoniacal odor, and readily soluble in water, alcohol and ether; the diethyl hydrazine boils at  $96-99^\circ$ .

Diethylhydrazine unites with ethyl iodide and yields the compound  $(\text{C}_2\text{H}_5)_3\text{N.NH}_2 \cdot \text{C}_2\text{H}_5\text{I}$  (triethylazonium iodide), which is to be viewed as the *ammonium*

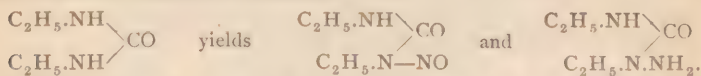
*iodide*,  $(\text{C}_2\text{H}_5)_3\text{N}^+\text{NH}_2 \text{I}^-$ . This is not decomposed by alkalis; moist silver

oxide converts it into a strong alkaline hydroxide. Nascent hydrogen (zinc and sulphuric acid) decomposes this iodide in the manner indicated in the following equation.—



This reaction is an additional proof that the ammonium compounds represent atomic derivatives of pentavalent nitrogen (*Annalen*, 199, 318). When mercuric oxide acts upon diethylhydrazine *tetrazone*,  $(\text{C}_2\text{H}_5)_2\text{N.N:N(C}_2\text{H}_5)_2$ , is formed. This is a strong basic liquid with an alliaceous odor.

**Ethyl Hydrazine**,  $(\text{C}_2\text{H}_5)\text{HN.NH}_2$ , is obtained from diethyl urea, through the nitroso and hydrazine compounds:—

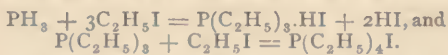


The latter, like all urea derivatives, decomposes, on boiling with acids or alkalis, into  $\text{C}_2\text{H}_5.\text{NH}_2$ ,  $\text{CO}_2$  and ethyl-hydrazine. The latter is very similar to diethylhydrazine, and boils at  $100^\circ$ . It reduces Fehling's solution in the cold. When ethyl hydrazine is acted upon by potassium disulphate, and the product treated with monopotassium carbonate, *potassium ethyl hydrazine sulphonate*,  $\text{C}_2\text{H}_5.\text{NH}-\text{NH.SO}_3\text{K}$ , is formed. Mercuric oxide changes this to *potassium diazo ethyl sulphonate*,  $\text{C}_2\text{H}_5.\text{N}=\text{N.SO}_3\text{K}$ . This is the only well known representative in the fatty-series of a numerous and highly important class of derivatives of the benzene series—the *diazo-compounds*. They are characterized by the *diazo group* — $\text{N}=\text{N}$ — which is on one side united with carbon radicals.

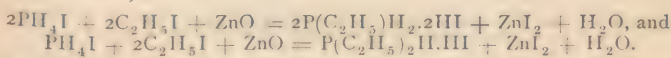
## PHOSPHINES OR PHOSPHORUS BASES.

Hydrogen phosphide,  $\text{PH}_3$ , has slight basic properties. Its compound with  $\text{HI}$ —phosphonium iodide,  $\text{PH}_4\text{I}$ —is not very stable. Through the introduction of alkyls (alcohol radicals), it acquires the strong basic character of ammonia; its derivatives—the phosphines or phosphorus bases—correspond perfectly to the amines.

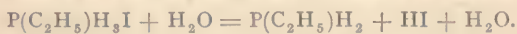
When the alkyl iodides act upon phosphine, tertiary phosphines and phosphonium iodides (Thénard) are the sole products:—



It is only recently that A. W. Hofmann has prepared the *primary* and *secondary* derivatives by letting the alkyl iodides act upon phosphonium iodide in the presence of certain metallic oxides, chiefly zinc oxide, the mixture being at the same time heated to about  $150^\circ$ . This procedure affords a mixture of the two classes (their  $\text{HI}$  salts):—

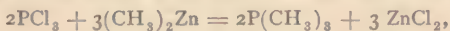


Water releases the monophosphine from the crystalline mass:—

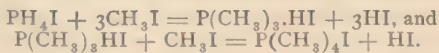


This is like the decomposition of  $\text{PH}_4\text{I}$  by water into  $\text{PH}_3$  and  $\text{HI}$ . The  $\text{HI}$  salt of the diethylphosphine is not affected. But by boiling the latter with sodium hydroxide, diethylphosphine is set free.

Thénard (1846) first discovered the tertiary phosphines by acting upon calcium phosphide with alkyl iodides. They also result when zinc alkyls are brought in contact with phosphorous chloride:



and upon heating alkyl iodides to  $100^\circ$  with amorphous phosphorus. The easiest course is to heat phosphonium iodide with alkyl iodides to  $150^\circ$ – $180^\circ$ , whereby phosphonium iodides are produced at the same time:—



If these be warmed with potassium hydrate, the tertiary phosphine is eliminated, while the iodide of the phosphonium base is unaltered (the case with the amines).

The phosphines are colorless, strongly refracting, extremely powerful-smelling, volatile liquids. They are nearly insoluble in water. On exposure to the air they are energetically oxidized and usually inflame spontaneously; hence, they must be prepared away

from air contact. With sulphur and carbon disulphide they combine readily. They form salts with the acids. Primary phosphines are very slightly basic, therefore, water decomposes their salts (see above).

### PRIMARY PHOSPHINES.

**Methyl Phosphine**,  $P(CH_3)H_2$ , is a gas, condensing at  $-20^\circ$  to a mobile liquid. It is readily soluble in alcohol and ether. Concentrated hydrochloric acid does not decompose its  $HCl$ -salt,  $P(CH_3)H_2.HCl$ ; it yields a double salt with platinic chloride. Fuming nitric acid oxidizes it to methyl phosphinic acid,  $CH_3.PO.(OH_2)$  (p.122).

**Ethyl Phosphine**,  $P(C_2H_5)H_2$ , boils at  $+25^\circ$  and swims upon water. It is very energetically oxidized by air contact, and ignites when brought near chlorine and bromine. Its platinum double salt consists of red needles.

**Isopropyl Phosphine**,  $P(C_3H_7)H_2$ , boils at  $41^\circ$ , and the **isobutyl** derivative,  $P(C_4H_9)H_2$ , at  $62^\circ$ .

### SECONDARY PHOSPHINES.

**Dimethyl Phosphine**,  $P(CH_3)_2H$ , boils at  $25^\circ C.$ , and takes fire on exposure to the air. Concentrated nitric acid converts it into dimethyl phosphinic acid,  $(CH_3)_2PO.OH$  (p.122).

**Diethyl Phosphine**,  $P(C_2H_5)_2H$ , boils at  $85^\circ$  and inflames spontaneously. Nitric acid oxidizes it to diethyl phosphinic acid,  $(C_2H_5)_2PO.OH$ .

**Di isopropyl Phosphine**,  $P(C_3H_7)_2H$ , boils at  $118^\circ$ . **Di isoamyl Phosphine**,  $P(C_5H_{11})_2H$ , boils at  $210^\circ-215^\circ$ , fumes in the air, but is not self-inflammable.

Water does not decompose the salts of the secondary phosphines. The  $HI$  salts and the double salts with platinic chloride are prepared with the least difficulty.

### TERTIARY PHOSPHINES.

**Trimethyl Phosphine**,  $P(CH_3)_3$ . In addition to the methods already described for the preparation of this compound, another may be employed, which consists in heating carbon disulphide with phosphonium iodide.

Trimethyl phosphine is a colorless, very disagreeably smelling liquid which will swim upon water. It boils at  $40^\circ$ . It fumes in the air, absorbing oxygen and igniting. When slowly oxidized it changes to trimethyl phosphine oxide,  $P(CH_3)_3O$ , which forms crystals that are deliquescent in the air. Sulphur will dissolve in the base and give a crystalline sulphide,  $P(CH_3)_3S$ . It combines in a like manner with the halogens, their hydrides, and also with  $CS_2$ . It yields salts with the acids, which are very soluble in water.

**Triethyl Phosphine**,  $P(C_2H_5)_3$ , is analogous to the above compound. It boils at  $127^\circ$ , and has a specific gravity of 0.812 at  $15^\circ$ . It has a neutral reaction. It dissolves slowly in acids, yielding salts. Its platinum double salt,  $[P(C_2H_5)_3.HCl]_2.PtCl_4$ , is difficultly soluble in water and crystallizes in red needles. It forms crystalline halogen derivatives,  $P(C_2H_5)_3.X_2$ .

**Triethyl Phosphine Oxide**,  $P(C_2H_5)_3O$ , results from the slow oxidation of phosphine in the air and also by the action of mercuric oxide:—



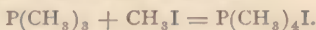
It forms deliquescent needles, melting at  $53^{\circ}$ , and distilling without decomposition at  $243^{\circ}$ . With the haloid acids it yields dihaloids, *e. g.*,  $P(C_2H_5)_3Cl_2$ , from which triethyl phosphine is regenerated on warming with sodium.

Triethyl phosphine dissolves sulphur to form a **sulphide**,  $P(C_2H_5)_3S$ , which crystallizes from water in brilliant needles, fusing at  $94^{\circ}$  and distilling about  $100^{\circ}$ . Mercury or lead oxide converts it into the oxide. Carbon disulphide also combines with triethyl phosphine, and the product is  $P(C_2H_5)_3.CS_2$ , crystallizing in red leaflets. It is insoluble in water, fuses at  $95^{\circ}$ , and sublimes without decomposition.

According to almost all these reactions, triethyl phosphine resembles a strongly positive bivalent metal; for example, calcium. By the addition of three alkyl groups, the pentavalent, metalloidal phosphorus atom acquires the character of a bivalent alkaline earth metal. By the further addition of an alkyl to the phosphorus in the phosphonium group,  $P(CH_3)_4$ , the former acquires the properties of a monovalent alkali metal. Similar conditions manifest themselves with sulphur, with tellurium, with arsenic, and also with almost all the less positive metals.

### PHOSPHONIUM BASES.

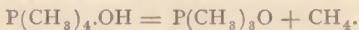
The tertiary phosphines combine with the alkyl iodides to form phosphonium iodides, which are not decomposed by alkalies:—



If, however, the iodides be treated with moist silver oxide the *phosphonium bases* result:—



These are perfectly analogous to the ammonium bases; they react alkaline, absorb carbon dioxide, and saturate the acids to form salts. When strongly heated they break up into phosphine oxide and hydrocarbons of the paraffin series:—



**Tetraethyl Phosphonium Iodide**,  $P(C_2H_5)_4I$ , consists of very soluble, white needles. When heated these decompose into  $P(C_2H_5)_3$  and  $C_2H_5I$ .

**Tetraethyl Phosphonium Hydroxide**,  $P(C_2H_5)_4.OH$ , is a crystalline compound that deliquesces on exposure. With acids it affords crystalline salts. The platinum double salt crystallizes in orange-red octahedra.

### ARSENIC BASES.

Arsenic is quite metallic in its character; its alkyl compounds fill out the gap between the nitrogen and phosphorus bases and the so-called metallo-organic derivatives, *i. e.*, the compounds of the alkyls with the metals (p. 139). The similarity to the amines and phosphines is observed in the existence of tertiary arsines,  $As(CH_3)_3$ , but these do not possess basic properties, nor do they unite with acids. They show in a marked degree the property of the tertiary phosphines, in their uniting with oxygen, sulphur and the halogens, to form compounds of the type  $As(CH_3)_3X_2$ . They yield *arsonium iodides* with the alkyl iodides:—





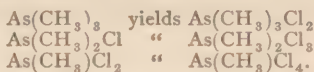
and these in turn become *hydroxides* by the action of moist silver oxide:—



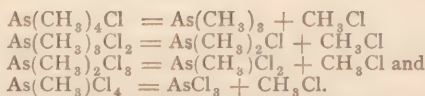
The hydroxides are analogous to the ammonium and phosphonium bases; they are very alkaline and, with acids, yield salts.

The arsines analogous to the *primary* and *secondary* amines and phosphines, such as  $\text{As}(\text{CH}_3)\text{H}_2$  and  $\text{As}(\text{CH}_3)_2\text{H}$ , are unknown, and probably cannot exist. Through an accumulation of alkyls, arsenic, like the metals, receives a more positive character;  $\text{As}(\text{CH}_3)_2\text{Cl}$  and  $\text{As}(\text{CH}_3)\text{Cl}_2$  act like the chlorides of the more positive metals.

By the acquisition of two halogen atoms the compounds of the form  $\text{AsX}_3$  pass into  $\text{AsX}_5$ :—



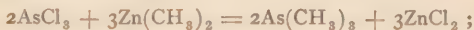
Heat converts these into the compounds of the form  $\text{AsX}_3$  and alkylgens:—



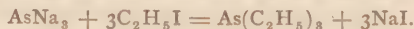
The decomposition is the more easy, the greater the number of the halogen atoms;  $\text{As}(\text{CH}_3)\text{Cl}_4$  breaks up at  $0^\circ$ , while  $\text{AsCl}_5$  has not been obtained.

### TERTIARY ARSINES AND ARSONIUM COMPOUNDS.

The tertiary arsines are formed by the action of the zinc alkyls upon arsenic trichloride:—



and also by heating the alkyl iodides with sodium arsenide:—



Cacodyl, formed simultaneously, is separated by fractional distillation.

**Trimethylarsine**,  $(\text{CH}_3)_3\text{As}$ . It is a colorless liquid, insoluble in water, and boils below  $100^\circ\text{C}$ . Its odor is very disagreeable. It fumes in the air, and absorbs oxygen, to form the oxide,  $\text{As}(\text{CH}_3)_3\text{O}$ , consisting of large deliquescent crystals. It also unites with the halogens and sulphur, forming  $\text{As}(\text{CH}_3)_3\text{Br}_2$  and  $\text{As}(\text{CH}_3)_3\text{S}$ , insoluble in water. At ordinary temperatures it combines with methyl iodide, forming **tetramethyl-arsonium iodide**,  $\text{As}(\text{CH}_3)_4\text{I}$ , which crystallizes from water in brilliant tables. Heat decomposes this last derivative into  $\text{As}(\text{CH}_3)_3$  and  $\text{CH}_3\text{I}$ . By the action of moist silver oxide **tetramethyl-arsonium hydroxide**,  $\text{As}(\text{CH}_3)_4\text{OH}$ , is obtained. This substance has a strongly alkaline reaction, is deliquescent, expels ammonia from its salts, and affords crystalline salts with the acids.

**Triethylarsine**,  $\text{As}(\text{C}_2\text{H}_5)_3$ , is a liquid difficultly soluble in water, and boiling at  $140^\circ$ , with partial decomposition. It fumes in the air, but only takes fire when heated. From its ethereal solution iodine precipitates the iodide,  $\text{As}(\text{C}_2\text{H}_5)_3\text{I}_2$ , a yellow amorphous substance. The oxide,  $\text{As}(\text{C}_2\text{H}_5)_3\text{O}$ , is a heavy oil, of disagreeable odor. It seems to combine to a salt with nitric acid. The sulphide,  $\text{As}(\text{C}_2\text{H}_5)_3\text{S}$ , is a crystalline substance, soluble in water.

**Tetraethyl-arsonium Iodide**,  $\text{As}(\text{C}_2\text{H}_5)_4\text{I}$ , is produced by the union of triethyl arsine and ethyl iodide. It is a crystalline compound, which forms an hydroxide,  $\text{As}(\text{C}_2\text{H}_5)_4\text{OH}$ , when treated with silver oxide. This is a strongly basic, deliquescent body, and with acids it yields salts. The platinum double salt consists of difficultly soluble, orange-red crystals.

### DIMETHYLARSINE COMPOUNDS.

The monovalent group,  $\text{As}(\text{CH}_3)_2$ , is strongly basic (see p. 134), and can form a series of derivatives, which, owing to their extremely disgusting odor, are termed *cacodyl compounds* (from *κακό* and *ὄδεν*):—

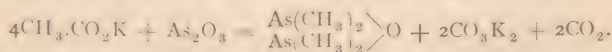
$\text{As}(\text{CH}_3)_2\text{Cl}$	Cacodyl chloride	$\text{As}(\text{CH}_3)_2$	
$\text{As}(\text{CH}_3)_2 > \text{O}$	Cacodyl oxide	$\text{As}(\text{CH}_3)_2$	Free cacodyl
$\text{As}(\text{CH}_3)_2 > \text{S}$	Cacodyl sulphide	$\text{As}(\text{CH}_3)_2 \cdot \text{CN}$	Cacodyl cyanide
		$\text{As}(\text{CH}_3)_2\text{O.OH}$	Cacodylic acid.

**Cacodyl Chloride**,  $\text{As}(\text{CH}_3)_2\text{Cl}$ , is formed by heating trimethyl arsen-dichloride,  $\text{As}(\text{CH}_3)_3\text{Cl}_2$  (see above), and by acting upon cacodyl oxide with hydrochloric acid. It is more readily obtained by heating the corrosive sublimate compound of the oxide with hydrochloric acid. It is a colorless liquid, boiling at about  $100^\circ$ , and possessing a stupefying odor. It acts like a chloride of the alkali metals, and yields an insoluble double salt with  $\text{PtCl}_4$ . It unites with chlorine to form the *trichloride*,  $\text{As}(\text{CH}_3)_2\text{Cl}_3$ , which decomposes at  $50^\circ$  already into  $\text{As}(\text{CH}_3)\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$ .

The bromide and iodide,  $\text{As}(\text{CH}_3)_2\text{I}$ , resemble the chloride, and are prepared in an analogous way.

**Cacodyl**,  $\text{As}_2(\text{CH}_3)_4 = \begin{array}{c} \text{As}(\text{CH}_3)_2 \\ | \\ \text{As}(\text{CH}_3)_2 \end{array}$ , Diarsentetramethyl. It is formed by heating the chloride with zinc in an atmosphere of  $\text{CO}_2$ . It is a colorless liquid, insoluble in water. It boils at  $170^\circ$ , and solidifies at  $-6^\circ$ . Its odor is frightfully strong, and may induce vomiting. Cacodyl takes fire very readily in the air and burns to  $\text{As}_2\text{O}_3$ , carbon dioxide and water. It yields cacodyl chloride with chlorine and the sulphide with sulphur. Nitric acid converts it into a nitrate,  $\text{As}(\text{CH}_3)_2\text{O.NO}_2$ .

**Cacodyl Oxide**,  $\text{As}(\text{CH}_3)_2 \begin{array}{c} \diagup \\ \diagdown \end{array} \text{O}$ , also termed *alcarsin*, is most easily made by distilling arsenic trioxide with potassium acetate:—

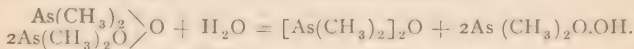


The distillate ignites spontaneously, because it contains some free cacodyl; the pure oxide does not act in this way.

Cacodyl oxide is a liquid with stupefying odor; it boils at  $150^\circ$ , and at  $-25^\circ$  solidifies to a scaly mass; its specific gravity at  $15^\circ$  is

1.462. It is insoluble in water, but dissolves very readily in alcohol and ether. It unites with acids to form salts, which are, however, purified with great difficulty. The sulphate appears to have the formula  $\text{SO}_2 \begin{smallmatrix} \diagup \text{O.As}(\text{CH}_3)_2 \\ \diagdown \text{O.As}(\text{CH}_3)_2 \end{smallmatrix}$ .

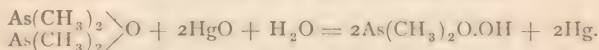
Slow oxidation converts the oxide into **cacodyl cacodylate**, which breaks up when distilled with  $\text{H}_2\text{O}$  into the oxide and cacodylic acid:—



**Cacodyl Sulphide**,  $\text{As}(\text{CH}_3)_2 \begin{smallmatrix} \diagup \text{As}(\text{CH}_3)_2 \\ \diagdown \text{S} \end{smallmatrix}$ , is obtained by distilling cacodyl chloride with barium hydrosulphide. It is an oily liquid insoluble in water and inflames in the air. Hydrochloric acid decomposes it into cacodyl chloride and  $\text{H}_2\text{S}$ . Sulphur dissolves in both it and cacodyl, forming the *disulphide*,  $[\text{As}(\text{CH}_3)_2]_2\text{S}_2$ , crystallizing in rhombic tables, which fuse at  $50^\circ$ .

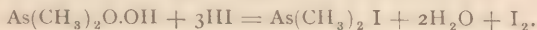
**Cacodyl Cyanide**,  $\text{As}(\text{CH}_3)_2.\text{CN}$ , is formed by heating cacodyl chloride with mercuric cyanide, or by the action of  $\text{CNH}$  upon cacodylic oxide. It crystallizes in glistening prisms, which fuse at  $37^\circ$ , and boil at  $140^\circ$ .

**Cacodylic Acid**,  $(\text{CH}_3)_2\text{AsO.OH}$  (see p. 122), (dimethyl-arsinic acid), is obtained by the action of mercuric oxide upon cacodylic oxide:—



It is easily soluble in water, and crystallizes in large prisms, which melt at  $200^\circ$ , with partial decomposition. Cacodylic acid is odorless, and appears to be non-poisonous. Its solution reacts acid and forms crystallizable salts with the metallic oxides, *e. g.*,  $(\text{CH}_3)_2\text{AsO.OAg}$ .

Hydriodic acid reduces the acid to iodide:—



Hydrogen sulphide changes it to sulphide.

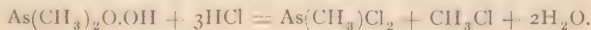
The salts of the thio cacodylic acid,  $(\text{CH}_3)_2\text{AsS.SH}$ , corresponding to cacodylic acid, are formed by the action of salts of the heavy metals upon cacodyl disulphide.

There are ethyl compounds analogous in constitution to the preceding methyl derivatives, but they have not been well investigated.

**Ethyl Cacodyl**,  $\text{As}(\text{C}_2\text{H}_5)_2 \begin{smallmatrix} \diagup \text{As}(\text{C}_2\text{H}_5)_2 \\ \diagdown \text{O} \end{smallmatrix}$ , diethylarsine, is formed together with triethylarsine on heating sodium arsenide with ethyl iodide. It is an oil, boiling at  $185\text{--}190^\circ$ , and takes fire in the air. When its alcoholic solution is permitted to slowly oxidize in the air, *diethyl arsinic acid*,  $(\text{C}_2\text{H}_5)_2\text{AsO.OH}$  (see p. 122), is produced; this crystallizes in deliquescent leaflets.

### MONOMETHYL ARSINE COMPOUNDS.

**Methylarsen-Dichloride**,  $\text{As}(\text{CH}_3)\text{Cl}_2$ , results in the decomposition of  $\text{As}(\text{CH}_3)_2\text{Cl}_3$  (p. 134) when heated, also by the distillation of cacodylic acid with hydrochloric acid:—



It is a heavy liquid, soluble in water, and boils at  $133^\circ$ . At  $-10^\circ$  it unites with

chlorine, forming  $\text{As}(\text{CH}_3)_3\text{Cl}_4$ , which at  $0^\circ$  breaks up into  $\text{AsCl}_3$  and  $\text{CH}_3\text{Cl}$ . From the alcoholic solution hydrogen sulphide precipitates the *sulphide*,  $\text{As}(\text{CH}_3)_3\text{S}$ , crystallizing in colorless needles, which melt at  $110^\circ$ .

When sodium carbonate acts upon the aqueous solution of the dichloride *methyl-arsenoxide*,  $\text{As}(\text{CH}_3)_3\text{O}$ , is formed. This is soluble, with difficulty, in water, and crystallizes from alcohol in colorless prisms, which fuse at  $95^\circ$ , and distil along with steam. The oxide is basic, and may be converted by the haloid acids and  $\text{H}_2\text{S}$  into the halogen derivatives,  $\text{AsCH}_3\text{X}_2$ , and the sulphide,  $\text{AsCH}_3\text{S}$ .

Silver oxide acting upon the aqueous solution of the above oxide changes it into the silver salt of mono-methyl arsenic acid,  $(\text{CH}_3)_3\text{AsO}(\text{OH})_2$ , an analogue of methyl phosphinic acid (p. 121). The free acid crystallizes in large plates, reacts acid, expels  $\text{CO}_2$  from carbonates, and combines with bases to yield salts, like  $(\text{CH}_3)_3\text{AsO}(\text{O.Ag})_2$ . Phosphorus pentachloride converts it into  $\text{As}(\text{CH}_3)_3\text{Cl}_2$ . When ethyl iodide acts upon sodium arsenite,  $\text{AsO}_3\text{Na}_3$  (p. 119), sodium mono-ethyl arsenate,  $\text{C}_2\text{H}_5\cdot\text{AsO}(\text{ONa})_2$ , is produced.

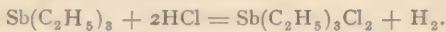
## ANTIMONY COMPOUNDS.

The derivatives of antimony and the alkyls are perfectly analogous to those of arsenic; but those containing one and two alkyl groups do not exist.

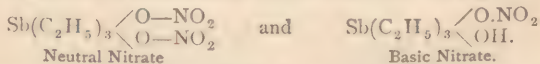
**Trimethylstibine**,  $\text{Sb}(\text{CH}_3)_3$ , antimony trimethyl, is obtained by heating methyl iodide with an alloy of antimony and potassium. It is a heavy liquid, insoluble in water, fuming and also taking fire in the air. It boils at  $80^\circ$ . It dissolves with difficulty in alcohol, but readily in ether. It forms compounds similar to those of triethyl stibine with the halogens and with oxygen. Antimony pentamethyl,  $\text{Sb}(\text{CH}_3)_5$ , is formed when zinc methyl- is permitted to act upon trimethyl stibine di-iodide. It is a liquid, and boils at about  $100^\circ$ . It does not ignite spontaneously.

Methyl iodide and trimethyl stibine unite and yield *tetramethylstibonium iodide*,  $\text{Sb}(\text{CH}_3)_4\text{I}$ , which crystallizes from water in beautiful tables. Warmed with moist silver oxide it passes into the hydroxide,  $\text{Sb}(\text{CH}_3)_4\cdot\text{OH}$ ,—a deliquescent, crystalline mass with strong alkaline reaction. The hydroxide affords beautifully crystallized salts with acids.

**Triethylstibine or Stibethyl**,  $\text{Sb}(\text{C}_2\text{H}_5)_3$ . This is perfectly analogous to the methyl derivative. In its reactions it manifests throughout the character of a bivalent metal, perhaps calcium or zinc (see p. 133). With oxygen, sulphur, and the halogens it combines energetically and decomposes the concentrated haloid acids, expelling their hydrogen:—



The dichloride,  $\text{Sb}(\text{C}_2\text{H}_5)_3\text{Cl}_2$ , is a thick liquid, having an odor like that of turpentine. The bromide solidifies at  $-10^\circ$ ; the iodide crystallizes in needles, fusing at  $70^\circ$ . Stibethyl slowly oxidized in the air becomes *triethylstibine oxide*,  $\text{Sb}(\text{C}_2\text{H}_5)_3\text{O}$ , an amorphous solid, soluble in water. It behaves like a di-acidic oxide, forming basic and neutral salts, which crystallize well, *e. g.*:—



**Triethylstibine Sulphide**,  $\text{Sb}(\text{C}_2\text{H}_5)_3\text{S}$ , is formed by the union of stibethyl and sulphur. It consists of shining crystals, melting at about  $100^\circ$ . It behaves somewhat like calcium sulphide. It dissolves readily in water, precipitates sul-



phides from solutions of the heavy metals and is decomposed by acids with the formation of hydrogen sulphide and salts of triethylstibine oxide.

*Tetraethylstibonium Iodide*,  $\text{Sb}(\text{C}_2\text{H}_5)_4\text{I}$ , is obtained from ethyl iodide and triethylstibine. It separates from water in large prisms. Silver oxide converts the iodide into *tetraethylstibonium hydroxide*,  $\text{Sb}(\text{C}_2\text{H}_5)_4\text{OH}$ , a thick liquid, reacting strongly alkaline and yielding well crystallized salts with acids.

## BORON COMPOUNDS.

**Triethylborine**, or Borethyl,  $\text{B}(\text{C}_2\text{H}_5)_3$ , is formed by the action of zinc ethyl upon boric ethyl ester (p. 121):—



It is a colorless, mobile liquid, of penetrating odor; its boiling point is  $95^\circ$ , and its sp. gr. at  $23^\circ$  equals 0.696. When heated together with hydrochloric acid it decomposes into diethylborine chloride and ethane:—



Slowly oxidized in the air triethylborine passes into the diethyl ester of ethyl boric acid or **Boron Etho-diethoxide**,  $\text{B}(\text{C}_2\text{H}_5)(\text{O}.\text{C}_2\text{H}_5)_2$ . This is a liquid boiling at  $125^\circ$ ; water decomposes it into alcohol and ethyl boric acid,  $\text{C}_2\text{H}_5\text{B}(\text{OH})_2$ . The latter is a crystalline, volatile body, which has a faintly acid reaction and is soluble in water, alcohol and ether.

*Bormethyl*, trimethylborine,  $\text{B}(\text{CH}_3)_3$ , is a colorless gas, that may be condensed by cold.

## SILICON COMPOUNDS.

The nearest analogue of carbon is silicon, therefore its derivatives with alcoholic radicals are very similar to the hydrocarbons.

**Silicon-methyl**,  $\text{Si}(\text{CH}_3)_4$ , is formed on heating  $\text{SiCl}_4$  with zinc methyl:—



It is a mobile liquid which boils at  $30^\circ$ . It is not changed by water, and behaves like a hydrocarbon (carbon tetramethane,  $\text{C}(\text{CH}_3)_4$ , boils at  $+10^\circ$ ).

**Silicon-Ethyl**, **Silicon Tetraethide**,  $\text{Si}(\text{C}_2\text{H}_5)_4$ , is similar to the preceding, and boils at  $153^\circ$ . By the action of chlorine there is formed a substitution product,  $\text{Si} \left\{ \begin{array}{l} (\text{C}_2\text{H}_5)_3 \\ \text{C}_2\text{H}_4\text{Cl} \end{array} \right.$ , boiling at  $185^\circ$ , which acts exactly like a chloride of a hydrocarbon. By the action of potassium acetate on this an acetic ester results:—



which alkalies decompose into acetic acid and the alcohol:—



This so-called **silico-nonyl alcohol** corresponds to nonyl alcohol,  $(C_2H_5)_3C.CH_2.CH_2OH$ . It boils at  $105^\circ$ , and is insoluble in water.

**Silicon Hexethyl**, or Hexethyl-silicoethane,  $Si_2(C_2H_5)_6$ , is formed by the action of zinc ethyl upon  $Si_2I_6$  (obtained from  $I_4Si$  by means of silver). It is a liquid, boiling from  $250-253^\circ$ .

On heating ethyl silicate,  $Si(O.C_2H_5)_4$  (p. 122), with zinc ethyl and sodium, the ethoxyl groups,  $(O.C_2H_5)$ , are successively replaced by ethyl groups. The product is a mixture of mono-, di- and triethylsilicon esters and silicon tetraethide, which are separated by fractional distillation.

**Triethylsilicon Ethylate**,  $(C_2H_5)_3Si.O.C_2H_5$ , is a liquid, boiling at  $153^\circ$ , insoluble in water, and having a sp. gr. 0.841 at  $0^\circ$ . Acetyl oxide converts it into the acetic ester, which, when saponified with potash, yields *triethylsilicon hydroxide*,  $(C_2H_5)_3Si.OH$ . The latter is sometimes called *triethylsilicol*; it is analogous to triethyl carbinol,  $(C_2H_5)_3C.OH$ , and deports itself like an alcohol. It is an oily liquid, insoluble in water.

**Diethylsilicon-diethylate**,  $(C_2H_5)_2Si.(O.C_2H_5)_2$ . An agreeable-smelling liquid, insoluble in water, and boiling at  $155.8^\circ$ . Its sp. gr. equals 0.875 at  $0^\circ$ . On treating it with acetyl chloride the compounds  $(C_2H_5)_2Si \begin{smallmatrix} O.C_2H_5 \\ \diagup \\ Cl \end{smallmatrix}$ , and  $(C_2H_5)_2SiCl_2$  are formed. The latter is a liquid, boiling at  $148^\circ$ . It fumes in air and with water yields diethylsilicon oxide,  $(C_2H_5)_2SiO$ , analogous to diethyl ketone,  $(C_2H_5)_2CO$ .

**Ethylsilicon-triethylate**,  $(C_2H_5)Si(O.C_2H_5)_3$ , is a liquid with a camphor-like odor, boiling at  $150^\circ$ , and decomposed slowly by water. Heated with acetyl chloride it forms ethyl silicon trichloride,  $(C_2H_5)SiCl_3$ . This liquid fumes strongly in the air, boils at about  $100^\circ$ , and when treated with water passes into ethyl silicic acid,  $(C_2H_5)Si(O.OH)_3$  (Silico-propionic acid), which is analogous to propionic acid,  $C_2H_5.CO.OH$ , in constitution. It is a white, amorphous powder, which on heating in the air becomes incandescent. It dissolves in potassium and sodium hydroxides to form salts.

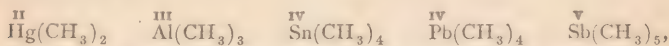
## METALLO-ORGANIC COMPOUNDS.

The metallo-organic compounds are those resulting from the union of metals with monovalent alkyls; those with the bivalent alkylens have not yet been prepared. Inasmuch as we have no marked line of difference between metals and metalloids, the metallo-organic derivatives attach themselves on the one side by the derivatives of antimony and arsenic, to the phosphorus and nitrogen bases; and on the other, through the selenium compounds to the sulphur alkyls and ethers. The tin derivatives approach the silicon alkyls and the hydrocarbons.

It is remarkable that only those metals are capable of yielding alkyl derivatives which, in accord with their position in the periodic system, attach themselves to the electro-negative metalloids. In the three large periods this power manifests and extends itself only as far as the group of zinc (Zn, Cd, Hg). (Compare *Inorganic Chemistry*.) The alkyl derivatives of potassium and sodium which cannot be isolated and are non-volatile, appear to possess a constitution

analogous to that of the hydrogen compounds,  $\text{Na}_2\text{H}$  and  $\text{K}_2\text{H}$ , or sodium acetylene,  $\text{C}_2\text{HNa}$ .

Those compounds, which correspond to the maximum valence of the metals, *e. g.*,

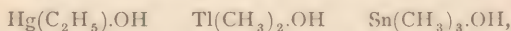


are volatile liquids, usually distilling undecomposed in vapor form; therefore, the determination of their vapor density is an accurate means of establishing their molecular weight and the valence of the metals. Being saturated compounds, they are incapable of taking up additional affinities.

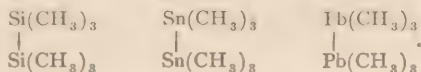
The behavior of the metallo-organic *radicals*, derived from the molecules by the separation of single alkyls, is especially noteworthy. The monovalent radicals, *e. g.*,



similar to all other monovalent radicals in that they cannot be isolated, show in all their derivatives great resemblance to the alkali metals. They yield hydroxides, *e. g.*,



which are perfectly similar to  $\text{KOH}$  and  $\text{NaOH}$ . On separating the monovalent radicals from their compounds, some can double themselves (derivatives of metals of the silicon group),—



By the exit of two alkyls from the saturated compounds, the bivalent radicals result:—

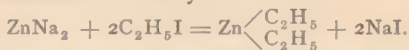


In their compounds (oxides and salts) these resemble the bivalent alkaline earth metals, or the metals of the zinc group. Just as we find with other radicals, some occur in free condition. As unsaturated molecules, however, they are highly inclined to saturate two affinities directly. Antimony triethyl,  $\text{Sb}(\text{C}_2\text{H}_5)_3$  (see p. 137), and apparently, too, tellurium diethyl,  $\text{Te}(\text{C}_2\text{H}_5)_2$ , have the power of uniting with acids to form salts, liberating hydrogen at the same time. This would indicate a distinct metallic character.

Finally, the trivalent radicals, like  $\overset{\text{V}}{\text{As}}(\text{CH}_3)_2$ , can also figure as monovalent. This is the case, too, with vinyl,  $\text{C}_2\text{H}_3$ . These may be compared to aluminium, and the so-called cacodylic acid,  $\text{As}(\text{CH}_3)_2\text{O}\cdot\text{OH}$  (p. 122), to aluminium meta-hydrate,  $\text{AlO}\cdot\text{OH}$ .

We conclude, therefore, that the electro-negative metals, by the successive union of alcohol radicals, always acquire a more strongly impressed basic, alkaline character. This also finds expression with the metalloids (sulphur, phosphorus, arsenic, etc. (Compare pp. 112 and 133.)) All the reactions of the alkyl compounds indicate that the various properties of the elementary atoms may be explained by the supposition of yet simpler primordial substances. (See Inorganic Chemistry.)

Most of the metallo-organic compounds can be prepared by the direct action of the metals or their sodium amalgams upon the bromides and iodides of the alkyls:—

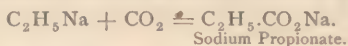


Derivatives of the electro-negative metals can be formed also from the metallic chlorides by the action of zinc and mercury alkyls:—



## COMPOUNDS OF THE ALKALI METALS.

When sodium or potassium is added to zinc methide or ethide, zinc separates at the ordinary temperature, and from the solution that is thus produced, crystalline compounds deposit on cooling. The liquid retains a great deal of unaltered zinc alkyl, but it also appears to contain the sodium and potassium compounds—at least it sometimes reacts quite differently from the zinc alkyls. Thus, it absorbs carbon dioxide, forming salts of the fatty acids:—

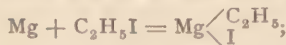


By the action of carbon monoxide, the ketones arise. These supposed alkali derivatives (p. 139) cannot be isolated, because when heat is applied to them, potassium and sodium separate and decomposition ensues. Their solutions are energetically oxidized in the air. Water decomposes them with extreme violence.

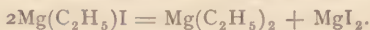
## COMPOUNDS OF THE METALS OF THE MAGNESIUM GROUP.

1. **Beryllium Ethide**,  $\text{Be}(\text{C}_2\text{H}_5)_2$ , is formed by heating beryllium with mercury ethyl. It is a colorless liquid, which boils from  $185^\circ$ – $188^\circ$ . It fumes strongly in the air and ignites spontaneously. Water decomposes it with violence, beryllium hydroxide,  $\text{Be}(\text{OH})_2$ , separating. **Beryllium Propyl**,  $\text{Be}(\text{C}_3\text{H}_7)_2$ , boils about  $245^\circ$ .

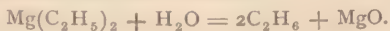
2. **Magnesium Ethide**,  $\text{Mg}(\text{C}_2\text{H}_5)_2$ . On warming magnesium filings with ethyl iodide away from contact with the air, magnesium ethyl iodide first results:



on applying heat to this it decomposes according to the following equation:—



Magnesium ethide is a liquid that takes fire on exposure to the air, and is decomposed by water with the production of ethane:—

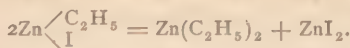


### 3. Zinc compounds.

The reaction observed above with magnesium may occur here,



*i. e.*, when zinc filings act upon iodides of the alcohol radicals in sunlight, iodides are formed, which decompose when heated :—



The dialkyl derivatives may be obtained by heating a solution of the alkyl iodides in absolute ether, with granulated zinc or zinc turnings, in closed vessels, to  $100^\circ$ – $120^\circ$  (Frankland).

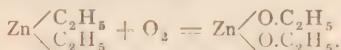
The reaction occurs at a lower temperature if an alloy of zinc and sodium be employed as a substitute for the metallic zinc. The operation is as follows: in a flask provided with a doubly perforated caoutchouc cork, bearing an inverted condenser, there is introduced a mixture of the alkyl iodide with ether and zinc sodium. The air is expelled from the vessel by a current of carbon dioxide, and heat of a water bath is then applied to it. When the reaction is complete, the condenser is reversed and the zinc compound distilled off in a current of  $\text{CO}_2$ .

Pure zinc turnings may replace the zinc sodium if they have been previously attacked by sulphuric acid and the pressure of the apparatus increased. This may be accomplished by connecting the inner tube of the condenser with another tube extending into mercury. The most convenient method of preparing zinc ethide is to let ethyl iodide act upon zinc-copper. (*Berichte*, 6, 200.)

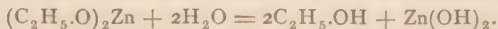
The zinc alkyls are colorless liquids, fuming strongly in the air and igniting readily; therefore, they can only be handled in a carbon dioxide atmosphere. They inflict painful wounds when brought in contact with the skin. Water decomposes them very energetically, forming hydrocarbons and zinc hydroxide :—



When slowly oxidized in the air (in ethereal solution), the zinc alcoholates are produced (see p. 96).



Water decomposes these into alcohols and zinc hydroxide :—

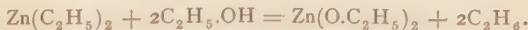


The free halogens decompose both the zinc alkyls and those of other metals very energetically :—



**Zinc Methide**,  $\text{Zn}(\text{CH}_3)_2$ , is a disagreeably smelling, mobile liquid, which boils at  $46^\circ$ . Its sp. gr. at  $10^\circ$  is 1.386.

**Zinc Ethide**,  $\text{Zn}(\text{C}_2\text{H}_5)_2$ , boils at  $118^\circ$ , and has the sp. gr. 1.182 at  $18^\circ$ . With alcohol it yields zinc alcoholate and ethane :—



It dissolves in sulphur, forming zinc mercaptide,  $\text{Zn}(\text{S.C}_2\text{H}_5)_2$ .

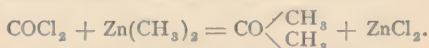
**Zinc Isoamyl**,  $\text{Zn}(\text{C}_3\text{H}_{11})_2$ , boils at  $220^\circ$ , fumes strongly in the air, but does not ignite spontaneously.

The zinc alkyls are very reactive, hence, serve for the preparation of many other compounds. Thus, they readily react with

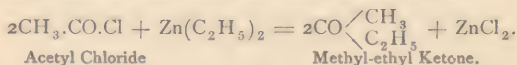
chlorides of the heavy metals and the metalloids, whereby alkyl derivatives of the latter are produced (p. 141). The hydrocarbons (see p. 46), are produced when they are heated to  $150^{\circ}$  with alkyl iodides:—



Carbon oxychloride converts them into ketones:—



The ketones are also produced in the action of the zinc alkyls upon the chlorides of the acid radicals in the cold:—

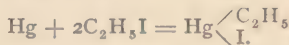


When an excess of the zinc alkyl is employed, tertiary alcohols are formed (p. 90).

The zinc alkyls absorb sulphur dioxide and become zinc salts of the sulphinic acids (p. 111). Nitric oxide dissolves in zinc diethyl and forms a crystalline compound, from which water and  $\text{CO}_2$  produce the zinc salt of the so-called dinitroethylic acid,  $\text{C}_2\text{H}_5\cdot\text{N}_2\text{O}_2\text{H}$ .

#### 4. Mercury compounds.

These are formed according to methods similar to those employed for the zinc compounds. The alkyl iodides unite with mercury at ordinary temperatures to yield iodides (sunlight is favorable):—



To get the dialkyl compounds, sodium amalgam is permitted to act upon the alkyl iodides:—



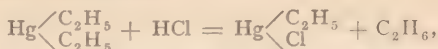
The reaction may be executed as follows: Liquid sodium amalgam is gradually added to a mixture of the iodide or bromide with  $\frac{1}{10}$  volume ethyl acetate, accompanied by frequent shaking of the vessel; the reaction occurs then with increase of heat. When the mass becomes syrupy, it is distilled, and the operation repeated until all the iodide is decomposed (until on boiling with  $\text{HNO}_3$ , iodine no longer separates). The oily distillate is shaken with potassium hydrate to decompose the ethyl acetate, the heavy oily mercury alkyl separated, and after drying with calcium chloride it is distilled. (*Annalen*, 103, 105 and 109.)

The action of zinc alkyls upon mercuric chloride also produces them:—

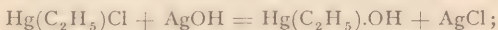


These compounds are colorless, heavy liquids, possessing a faint, peculiar odor. Their vapors are extremely poisonous. Water and air occasion *no* change in them, but when heated they ignite easily.

The haloid acids cause one alkyl group to split off, leaving salts of the monoalkyl derivatives:—

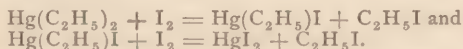


and when moist silver oxide acts on the halogen derivatives, *hydroxyl* compounds are produced:—



these are strongly alkaline, and form crystalline salts with the acids.

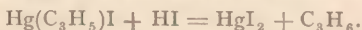
One and two alkyls separate from the mercury alkyls by the action of the halogens:—



**Mercury-Methyl**,  $\text{Hg}(\text{CH}_3)_2$ , is a liquid having a specific gravity of 3.069; it boils at  $95^\circ$ , and is but slightly soluble in water. When a molecule of iodine is added to its alcoholic solution there is formed mercury methyl iodide,  $\text{Hg}(\text{CH}_3)\text{I}$ , insoluble in water, but soluble in alcohol, from which it crystallizes in shining leaflets, which fuse at  $143^\circ$ . Potassium cyanide converts the iodide again into mercury-methyl. When treated with silver nitrate the salt,  $\text{Hg}(\text{CH}_3).\text{O.NO}_2$ , is produced.

**Mercury Ethide**,  $\text{Hg}(\text{C}_2\text{H}_5)_2$ , has a specific gravity of 2.44, and boils at  $159^\circ$ . At  $200^\circ$  it decomposes into  $\text{Hg}$  and  $\text{C}_4\text{H}_{10}$ . Its *chloride*,  $\text{Hg}(\text{C}_2\text{H}_5)\text{Cl}$ , separates in brilliant needles, when its alcoholic solution is digested with  $\text{HgCl}_2$ . Direct sunlight decomposes the *iodide* into  $\text{Hg}$  and  $\text{C}_4\text{H}_{10}$ . These halogen derivatives when treated with moist silver oxide, yield *mercury ethyl hydroxide*,  $\text{Hg}(\text{C}_2\text{H}_5).\text{OH}$ , a thick liquid of strong alkaline reaction, and soluble in both water and alcohol. It forms crystalline salts with the acids.

**Mercury-Allyl Iodide**,  $\text{Hg}(\text{C}_3\text{H}_5)_2\text{I}$ , is obtained when allyl iodide is shaken with mercury. It crystallizes from alcohol in shining leaflets, fusing at  $135^\circ$ . Propylene results when hydriodic acid acts on the iodide:—



## COMPOUNDS OF THE METALS OF THE ALUMINIUM GROUP.

The aluminium alkyl derivatives attach themselves to those springing from boron (p. 138); however, it appears that only those exist in which three alkyls are present. They are produced by the action of the mercury alkyls upon aluminium filings:—



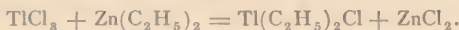
**Aluminium-Methyl**,  $\text{Al}(\text{CH}_3)_3$ , boils at  $130^\circ$ , and crystallizes at  $0^\circ$ . It fumes in the air, and is spontaneously inflammable. Water decomposes it with great violence, forming ethane and aluminium hydrate. Its vapor density has been found to be 2.8 (or 35.6,  $\text{H} = 1$ ) at  $240^\circ$ ; this would answer to the molecular formula  $\text{Al}(\text{CH}_3)_3 = 72.3$ . It, however, appears that at low temperatures the molecules  $\text{Al}_2(\text{CH}_3)_6$  also exist.

**Aluminium-Ethyl**,  $\text{Al}(\text{C}_2\text{H}_5)_3$ , is perfectly analogous to the preceding compound, but does not solidify in the cold. It boils at  $194^\circ$ . At  $240^\circ$  its vapor density has been found equal to 4.5 (or 64,  $\text{H} = 1$ ), almost corresponding to the molecular formula  $\text{Al}(\text{C}_2\text{H}_5)_3 = 114.3$ .

The derivatives of trivalent gallium and indium have not been prepared.

Two thallium-diethyl compounds,  $\text{Tl}(\text{C}_2\text{H}_5)_2\text{X}$ , are known.

**Thallium-Diethyl Chloride**,  $\text{Tl}(\text{C}_2\text{H}_5)_2\text{Cl}$ , is formed when zinc ethide is allowed to act upon thallium chloride:—

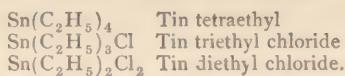


Thallium-diethyl salts, *e. g.*,  $\text{Tl}(\text{C}_2\text{H}_5)_2\text{O}.\text{NO}_2$ , are obtained from this by double decomposition with silver salts. If the sulphate be decomposed with barium hydrate, *thallium-diethyl hydroxide*,  $\text{Tl}(\text{C}_2\text{H}_5)_2.\text{OH}$ , is obtained. This is readily soluble in water, crystallizes therefrom in glistening needles, and has a strong alkaline reaction.

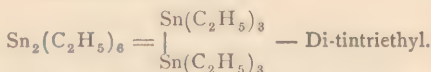
## COMPOUNDS OF TIN AND LEAD.

The alkyl derivatives of these two elements are analogous in constitution to those of silicon (p. 138) belonging to the same group; their differences in reaction are induced by the more positive, metallic nature of tin and lead (see p. 140).

In addition to the saturated derivatives with four alkyls, *tin* is also capable of uniting with three and two alkyls to groups which act like *basic radicals*, forming salt-like compounds with negative groups:—



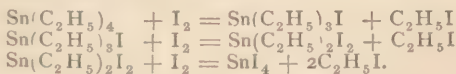
Tin diethyl,  $\text{Sn}(\text{C}_2\text{H}_5)_2$ , appears to exist as an unsaturated molecule (like tin dichloride,  $\text{SnCl}_2$ ), while the group,  $\text{Sn}(\text{C}_2\text{H}_5)_3$ , in free condition doubles itself:—



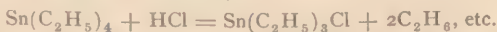
**Tin Tetraethyl, Stannic Ethide**,  $\text{Sn}(\text{C}_2\text{H}_5)_4$ , is best prepared by distilling tin chloride with zinc ethyl:—



It is a colorless, ethereal smelling liquid, boiling at  $181^\circ$  and possessing a specific gravity of 1.187 at  $23^\circ$ . Its vapor density equals 8.02 or 116 ( $\text{H} = 1$ ). It is insoluble in water and does not suffer change on exposure to the air. By the action of the halogens the alkyls are successively eliminated:—



Hydrochloric acid acts similarly:—



**Tin Tetramethyl**,  $\text{Sn}(\text{CH}_3)_4$ , is similar to the preceding, boils at  $78^\circ$ , and has a specific gravity at  $0^\circ$  of 1.314.



On heating an alloy of tin and a little sodium (about 2 per cent.) with ethyl iodide, there results a mixture consisting of  $\text{Sn}(\text{C}_2\text{H}_5)_3\text{I}$  and  $\text{Sn}(\text{C}_2\text{H}_5)_2\text{I}_2$ , which may be separated by fractionation. With an alloy rich in sodium (about 20 per cent) the products are  $\text{Sn}(\text{C}_2\text{H}_5)_2$  and  $\text{Sn}_2(\text{C}_2\text{H}_5)_6$ ; the latter is almost insoluble in alcohol, while the first is very soluble and can be re-precipitated by water.

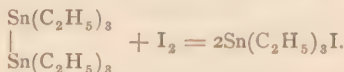
**Tin-Triethyl Iodide**,  $\text{Sn}(\text{C}_2\text{H}_5)_3\text{I}$ , is a colorless oil, insoluble in water, and having a disagreeable smell. It boils at  $231^\circ$ , and has a specific gravity of 1.83; at  $22^\circ$ . Hydrochloric acid precipitates the *chloride*,  $\text{Sn}(\text{C}_2\text{H}_5)_3\text{Cl}$ , from tin triethyl salts, as a heavy oil, which solidifies at  $0^\circ$ . It boils from  $208$ – $210^\circ$ , and has a specific gravity of 1.428. Alcohol is a solvent for both. When either one is acted upon by silver oxide or caustic potash, there is produced:—

**Tin-Triethyl Hydroxide**,  $\text{Sn}(\text{C}_2\text{H}_5)_3\text{OH}$ , which crystallizes in shining prisms, melting at  $66^\circ$ , and boiling undecomposed at  $272^\circ$ . It volatilizes along with the steam. Difficultly soluble in water, it dissolves readily in alcohol and ether. It reacts strongly alkaline, absorbs carbon dioxide, and affords crystalline salts with the acids, *e. g.*,  $\text{Sn}(\text{C}_2\text{H}_5)_3\text{O}\cdot\text{NO}_2$ . When the hydroxide is heated for some time to almost the boiling temperature, it breaks up into water and *tin-triethyl oxide*,  $\text{Sn}(\text{C}_2\text{H}_5)_3\text{O}$ , an oily liquid, which in the presence of water at once regenerates the hydrate.

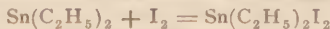
Free Tin-Triethyl,  $\begin{array}{c} \text{Sn}(\text{C}_2\text{H}_5)_3 \\ | \\ \text{Sn}(\text{C}_2\text{H}_5)_3 \end{array} = \text{Sn}_2(\text{C}_2\text{H}_5)_6$ , or *Stannoso-stannic Ethide*, is produced, as already described, by heating tin-sodium with ethyl iodide; also on warming tin-triethyl iodide with sodium:—



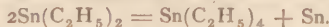
It is a liquid, of mustard like odor, insoluble in alcohol, but readily soluble in ether. It distils with slight decomposition at  $265$ – $270^\circ$ . It combines with oxygen, forming tin-triethyl oxide,  $\begin{array}{c} \text{Sn}(\text{C}_2\text{H}_5)_3 \\ | \\ \text{Sn}(\text{C}_2\text{H}_5)_3 \end{array} \text{O}$ , and with iodine yielding tin-triethyl iodide:—



**Tin-Diethyl**, or **Stannous Ethide**,  $\text{Sn}(\text{C}_2\text{H}_5)_2$ . Its preparation is described above. It is a thick oil, decomposing when distilled, therefore its molecular weight has not been determined. It combines with oxygen and the halogens:—



When distilled it decomposes completely into tin and tin-tetraethyl:—



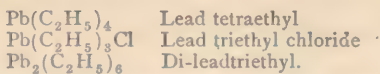
**Tin-Diethyl Chloride**,  $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ , is best prepared by dissolving tin-diethyl oxide in hydrochloric acid. It is insoluble in water, alcohol and ether, crystallizes in needles, fusing at  $63^\circ$ , and boils at  $220^\circ$ . The iodide,  $\text{Sn}(\text{C}_2\text{H}_5)_2\text{I}_2$ , is also produced by the action of ethyl iodide in sunlight upon zinc filings. It crystallizes in needles, fuses at  $44.5^\circ$ , and boils at  $245^\circ$ .

Ammonium hydrate and the alkalis precipitate from aqueous solutions of both the halogen compounds:—

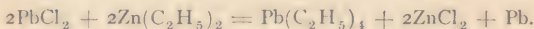
**Tin-Diethyl Oxide**,  $\text{Sn}(\text{C}_2\text{H}_5)_2\text{O}$ , a white, insoluble powder. It is soluble in excess of alkali, and forms crystalline salts with the acids, *e. g.*,  $\text{Sn}(\text{C}_2\text{H}_5)_2 \begin{array}{c} \diagup \text{O}\cdot\text{NO}_2 \\ \diagdown \text{O}\cdot\text{NO}_2 \end{array}$ .

## LEAD COMPOUNDS.

These are very similar to the preceding; derivatives with two alkyls do not, however, exist:—

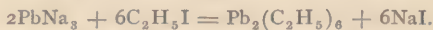


**Lead-Tetraethyl**,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , is obtained by heating lead chloride with zinc ethide:—

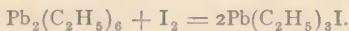


It is an oily liquid, distilling out of air contact at about  $200^\circ$ , with partial decomposition. When heated in the air it takes fire and burns with an orange colored flame. When hydrogen chloride acts upon it, ethane is evolved and *Lead Triethyl chloride*,  $\text{Pb}(\text{C}_2\text{H}_5)_3\text{Cl}$ , formed, which crystallizes in silky, shining needles. The *iodide*,  $\text{Pb}(\text{C}_2\text{H}_5)_3\text{I}$ , is very similar to the last, and is produced when iodine acts upon lead-tetraethyl. On heating either of these derivatives with silver oxide or caustic potash, *lead-triethyl hydroxide*,  $\text{Pb}(\text{C}_2\text{H}_5)_3\text{OH}$ , distils over. This reacts very alkaline, and forms crystalline salts with the acids. The sulphate,  $[\text{Pb}(\text{C}_2\text{H}_5)_3]_2\text{SO}_4$ , is soluble in water with difficulty.

**Lead-Triethyl**,  $\text{Pb}_2(\text{C}_2\text{H}_5)_6$ , is obtained by the action of ethyl iodide on an alloy of lead and sodium:—



Lead-triethyl is a yellowish liquid, insoluble in water, possessing a sp. gr. of 1.471 at  $10^\circ$ , and boiling with partial decomposition. It reacts energetically with the halogens:—



The lead-methyl derivatives are perfectly analogous to the ethyl compounds.

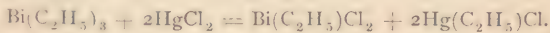
## COMPOUNDS OF BISMUTH.

These arrange themselves with those derived from antimony and arsenic; but in accordance with the complete metallic nature of bismuth, we do not meet any compounds here analogous to stibonium (p. 138) or arsonium.

**Bismuth-Triethyl**,  $\text{Bi}(\text{C}_2\text{H}_5)_3$ , is formed by acting upon an alloy of bismuth and potassium (obtained by igniting crude tartar and bismuth) with ethyl iodide. It is a mobile, disagreeable-smelling liquid, with a specific gravity of 1.8200. It is insoluble in water, but readily dissolved by ether. It fumes in the air and inflames spontaneously. When heat is applied it decomposes below  $100^\circ$ . It reacts very energetically with the halogens, according to the equation:—



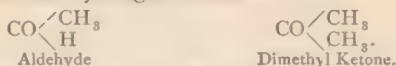
**Bismuth-ethyl Chloride**,  $\text{Bi}(\text{C}_2\text{H}_5)\text{Cl}_2$ , is formed when mercuric chloride acts on bismuth-triethyl:—



The *iodide*,  $\text{Bi}(\text{C}_2\text{H}_5)\text{I}_2$ , results when the chloride is warmed with KI. This salt crystallizes in yellow leaflets. From its alcoholic solution the alkalis precipitate *Bismuth-ethyl oxide*,  $\text{Bi}(\text{C}_2\text{H}_5)\text{O}$ , an amorphous, yellow powder, which takes fire readily in the air. The *nitrate*,  $\text{Bi}(\text{C}_2\text{H}_5)\begin{smallmatrix} \text{O.NO}_2 \\ \text{O.NO}_2 \end{smallmatrix}$ , is produced by adding silver nitrate to the iodide. This crystallizes from alcohol, explodes on being warmed, and is decomposed by water with formation of bismuth dinitrate,  $\text{Bi}(\text{OH})(\text{NO}_3)_2$ .

## ALDEHYDES AND KETONES.

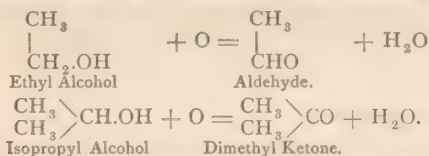
Aldehydes and ketones contain the carbonyl group CO, which in the latter unites two alkyls, but in the former is combined with only one alkyl and one hydrogen atom :—



This expresses the similarity and the difference in character of aldehydes and ketones.

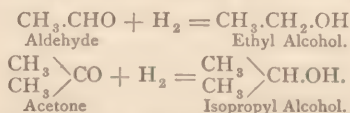
The methods of preparation common to both classes of compounds are :—

1. Oxidation of the alcohols, whereby the primary alcohols change to aldehydes and the secondary to ketones (see p. 88) :—

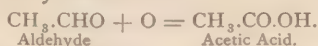


The above oxidation may be effected by oxygen; or air in presence of platinum sponge, or by ozone. It takes place more readily on warming the alcohols with potassium dichromate (or  $\text{MnO}_2$ ) and dilute sulphuric acid; to prevent the oxidation extending too far, it is sometimes recommended to employ an aqueous solution of chromic acid (*Ber.*, 5, 699).

Conversely, aldehydes and ketones by an addition of hydrogen again become primary and secondary alcohols :—

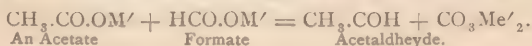


Further oxidation converts the aldehydes into acids, but the ketones suffer decomposition by means of it :—

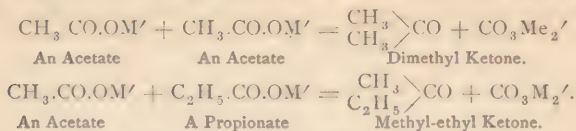


Empirically the aldehydes are distinguished from the alcohols by possessing two atoms less of hydrogen—hence their name (from *Alkohol dehydrogenatus*), e. g., ethyl aldehyde, propyl aldehyde, etc., etc. On account of their intimate relationship to the acids, their names are also derived from the latter, like acetaldehyde, propionic aldehyde, etc.

2. The dry distillation of a mixture of the calcium, or better, barium salts of two monobasic fatty acids. Should in this case one of the acids be formic acid, aldehydes are produced :—



In all other instances ketones result, and they are either *simple*, with two similar alkyls, or *mixed*, with two dissimilar alkyls:—

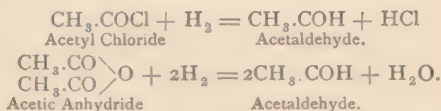


When working with higher, more difficultly volatilized aldehydes and ketones it is advisable to distil in vacuo (see p. 38).

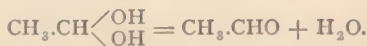
Both aldehydes and ketones combine with primary alkaline sulphites, yielding crystalline compounds (see later).

## ALDEHYDES.

The aldehydes, *e. g.*, acetaldehyde,  $\text{CH}_3 \cdot \text{CHO}$ , are compounds containing the group  $\text{COH}$ , which is readily formed by the oxidation of the primary alcoholic group,  $\text{CH}_2 \cdot \text{OH}$  (p. 148). Again, corresponding to their fatty acid origin aldehydes may be viewed as the hydrogen derivatives of the *acid radicals*. This would explain their formation by the action of nascent hydrogen (sodium amalgam) upon the chlorides of acid radicals or their oxides (the acid anhydrides):—



Hence, they may be comprehended as the oxides of bivalent radicals (like  $\text{CH}_3 \cdot \text{CH} = \text{ethidene}$ ), or as the anhydrides of the very unstable dihydroxyl derivatives of these. Wherever the formation of these latter compounds occurs we can expect, from their close analogy to the glycols, that water will split off and the aldehydes result:—



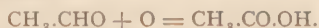
This explains the formation of *e. g.*, acetaldehyde (ethidene oxide) from ethidene chloride,  $\text{CH}_3 \cdot \text{CHCl}_2$ , when heated with water (more readily in presence of lead oxide), and also its production from the ethereal and ester-like compounds, such as ethidene diacetate,  $\text{CH}_3 \cdot \text{CH}(\text{O} \cdot \text{C}_2\text{H}_3\text{O})_2$ , by saponification with alkalis or sulphuric acid. In a similar manner, on heating glycollic and lactic acids,  $\text{CH}_2 \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$ ,  $\text{CH}_3 \cdot \text{CH} \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$ , with acids, there occurs a splitting-off of formic acid (or of  $\text{CO}$  and  $\text{H}_2\text{O}$ ) and the products are methylene oxide,  $\text{CH}_2\text{O}$  (formic aldehyde), acetaldehyde,  $\text{CH}_3 \cdot \text{CHO}$ , etc.

Besides these general methods the aldehydes, as the transitional members to the acids, frequently appear in the oxidation (by means



of manganese peroxide and dilute sulphuric acid or a chromic acid solution) of complex substances such as the albuminoids.

The aldehydes exhibit in their properties a gradation similar to that of the alcohols. The lower members are volatile liquids, soluble in water, and have a peculiar odor, but the higher are solids, insoluble in water, and cannot be distilled without decomposition. In general they are more volatile and more difficultly soluble in water than the alcohols. In chemical respects the aldehydes are neutral substances, yet they are easily oxidized to acids on exposure to the air:—

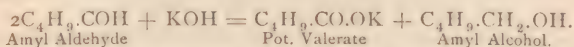


Their ready oxidation by the oxides and salts of the noble metals (the latter being separated in free condition) is characteristic of aldehydes. On adding an aqueous aldehyde solution to a weak ammoniacal silver nitrate solution, silver separates on the sides of the vessel as a brilliant mirror.

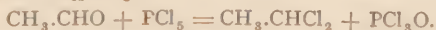
The reaction is more delicate in the presence of caustic potash (*Ber.*, 15, 1635 and 1828); such a solution will even reduce cane sugar and glycerol when assisted by heat. Alkaline copper solutions are reduced, too, by many fatty aldehydes (*B. r.*, 14, 675 and 1950). The reduction of alkaline silver and copper solutions is, however, not peculiar to the aldehyde groups alone, but belongs also to some other atomic groups (see acetone alcohol, glycid alcohol, hydrazine). A very delicate reaction of the aldehydes is their power of imparting an intense violet color to a fuchsine solution previously decolorized by sulphurous acid (*Berichte*, 14, 1848). Chloral hydrate and the glucoses do not, but some ketones do, show this reaction (*Ber.*, 14, 791). The following is more sensitive: Add an aldehyde and a little sodium amalgam to the sodium hydrate solution of diazobenzene sulphonic acid and a violet-red coloration is produced. Grape sugar, but not chloral, will do the same. Acetone and acetic ether afford a dark red coloration (*Ber.*, 16, 657).

When oxygen or air is conducted through the hot solution of an aldehyde (like paraldehyde) in alcoholic potash, an intense light-display is observed; many aldehyde derivatives and even grape sugar deport themselves similarly (*Berichte*, 10, 321).

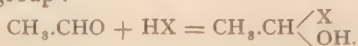
Nearly all the aldehydes are converted into resin by the alkalies; some are transformed into acids and alcohols by alcoholic alkali solutions:—



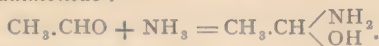
Phosphorus pentachloride replaces the oxygen of aldehyde by two chlorine atoms (p. 65):—



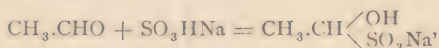
Notwithstanding they are really saturated compounds, aldehydes possess in a remarkable degree the property of uniting two affinities directly, and thereby changing the oxygen united with two affinities to the hydroxyl group:—



Thus they become alcohols by addition of two hydrogen atoms. They unite directly with ammonia to form crystalline compounds, called *aldehyde-ammonias* :—

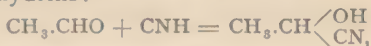


These are readily soluble in water, but not in ether, hence ammonia gas will precipitate them in crystalline form from the ethereal solution of the aldehydes. They are rather unstable and dilute acids again resolve them into their components. Aldehydes unite in a similar manner with acid alkaline sulphites, forming crystalline compounds :—



which may be regarded as salts of *oxysulphonic acids*. The aldehydes may be released from these salts by distillation with dilute sulphuric acid or soda. This procedure permits the separation and purification of aldehydes from other substances.

Aldehydes also combine with hydrogen cyanide, yielding *oxycyanides* or *cyanhydrins* :—

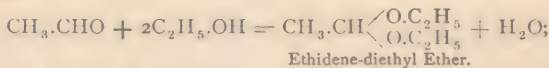


from which oxyacids are prepared.

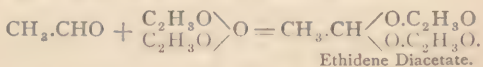
These cyanides, which are often crystalline, may be prepared by prolonged heating of the aldehydes with a concentrated CNH solution, or by adding hydrochloric acid to a mixture of the aldehyde and pulverized potassium cyanide (*Berichte*, 14, 235 and 1965). When these compounds are distilled they usually break up into their components. The alkalis also cause a separation of CNH. When hydrochloric or sulphuric acid acts upon them they pass into oxyacids.

With ammonium cyanide aldehydes form *amidocyanides*, like  $\text{CH}_3.\text{CH} \begin{smallmatrix} \text{NH}_2 \\ \text{CN} \end{smallmatrix}$ , which yield amido-acids (see these).

Being the oxides of the radicals,  $\text{R}.\text{CH}=\text{}$  (p. 149), aldehydes can, by direct additions, form ether and ester derivatives. Thus they combine at  $100^\circ$  with the alcohols and build the so-called *acetals* :—



and with the acid anhydrides they yield esters :—



These compounds will be treated with the derivatives of the bivalent radicals.

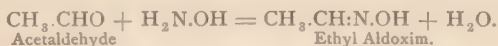
The *polymerization* of the aldehydes depends upon a similar partial separation of the oxygen atoms and the union through the latter

of several aldehyde radicals,  $\text{CH}_3\text{CH}=\text{}$ . This occurs especially with the lower members of the series. Thus from formic aldehyde,  $\text{CH}_2\text{O}$ , arises trioxymethylene,  $(\text{CH}_2\text{O})_3$ , from acetaldehyde,  $\text{C}_2\text{H}_4\text{O}$ , paraldehyde,  $(\text{C}_2\text{H}_4\text{O})_3$ , and metaldehyde,  $(\text{C}_2\text{H}_4\text{O})_n$  (see p. 154).

The readiness with which the polymerides break up into simple molecules shows that in them the carbon atoms are not in union with each other; their power of refracting light (p. 40) would also indicate this (*Annalen*, 203, 44).

Finally, the aldehydes *condense* readily, *i. e.*, two molecules unite by means of two carbon atoms and water may or may not separate (aldehyde and aldol condensation, see p. 154).

By such an exit of water the aldehydes (also the ketones) are endowed with the power of entering into combination with free hydroxylamine (or its HCl-salt) and forming the so-called **aldoxims** (acetoxims) (V. Meyer):—



These contain the bivalent *oximid* group,  $\text{N}\cdot\text{OH}$ , combined with one carbon atom. They are isomerides of the nitroso-compounds (see p. 78), hence also designated the *isonitroso-derivatives* of the hydrocarbons. The aldoxims are, as a usual thing, liquid bodies that boil without decomposition. Ethers are produced when the hydrogen of their hydroxyl group is replaced by acid radicals or by the alkali metals (by means of sodium alcoholate) and the alkyls. When boiled with acids they are again changed to aldehyde and hydroxylamine.

The aldoxims result from all compounds which, like the aldehydes, contain the aldehyde group,  $\text{CHO}$ , *e. g.*, the aldehyde acids (*Berichte*, 15, 2783, 16, 823 and 1780). Paraldehyde and metaldehyde (see above) do not react with hydroxylamine. All the ketones and compounds containing the group  $\text{CO}$  peculiar to them yield corresponding *acetoxims* (see Ketones). These oximido- or isonitroso-derivatives do not show the nitroso reaction (see p. 79).

All the aldehydes (also the ketones) react more readily with phenyl hydrazine (*Ber.*, 16, 661, 17, 574) than with hydroxylamine.

## I. ALDEHYDES OF THE PARAFFIN SERIES, $\text{C}_n\text{H}_{2n}\text{O}$ .

**1. Methyl Aldehyde**,  $\text{CH}_2\text{O}$ , also called **Formic Aldehyde**, or oxymethylene, is only known in aqueous solution and in gaseous form. It arises in the oxidation of methyl alcohol, if its vapors mixed with air be conducted over an ignited platinum spiral; also by the distillation of calcium formate. Its aqueous solution, containing methyl alcohol, possesses a penetrating odor, and reduces an ammoniacal silver nitrate solution. When heat is applied the aldehyde escapes, a portion of it, however, polymerizes to solid **paraformaldehyde** (see p. 153).

Formic aldehyde appears to exist in the plant cells which contain chlorophyll (*Berichte*, 14, 2147).

A ready method for producing it consists in conducting a mixture of air and the vapors of methyl alcohol over platinized asbestos heated in a glass tube (*Berichte*, 15, 1448, 16, 917). When digested with ammonia water the aldehyde becomes hexamethylene-amine,  $(\text{CH}_2)_6\text{N}_4$ , from which it may be regenerated by distilling with dilute sulphuric acid (*Berichte*, 16, 1333). Formic aldehyde is converted into formic acid when boiled with alkalis. Formic acid and halogen derivatives of methane are the products of the action of haloid acids at  $100^\circ$  upon this aldehyde:  $2\text{CH}_2\text{O} + \text{HBr} = \text{CH}_2\text{O}_2 + \text{CH}_3\text{Br}$  (*Ber.*, 16, 2287).

**Paraformaldehyde**,  $(\text{CH}_2\text{O})_3$ , **Trioxymethylene**, is obtained by the action of silver oxide or oxalate upon methene di-iodide, or by heating methene di-acetyl ester,  $\text{CH}_2(\text{O}.\text{C}_2\text{H}_3\text{O})_2$ , with water, to  $100^\circ$ . It is best prepared by distilling glycollic acid or calcium diglycollate with a little concentrated sulphuric acid (*Annalen*, 138, 43). It is a white, crystalline mass, insoluble in water, alcohol and ether, and when heated gives out an irritating smell. It fuses at  $152^\circ$ , and sublimes below  $100^\circ$ . The vapors have the formula  $\text{CH}_2\text{O}$  which corresponds to their density. When cooled they again condense to the trimolecular form. When paraformaldehyde is heated with water to  $130^\circ$  it changes to the simple molecule  $\text{CH}_2\text{O}$ .

When hydrogen sulphide is conducted into the aqueous solution of  $\text{CH}_2\text{O}$  or over  $(\text{CH}_2\text{O})_3$ , the product is *Parathioformaldehyde*,  $(\text{CH}_2\text{S})_3$ . This compound is also produced when zinc and hydrochloric acid act upon carbon disulphide and by heating methene di-iodide,  $\text{CH}_2\text{I}_2$ , with alcoholic potassium sulphide. This compound possesses a leek like odor, is insoluble in water, and crystallizes from alcohol in fine needles, fusing at  $216^\circ$ , and subliming readily. The vapor density answers to the formula  $\text{C}_3\text{H}_6\text{S}_3$ , from which we infer that the triple formula,  $\text{C}_3\text{H}_6\text{O}_3$ , is to be ascribed also to paraformaldehyde. When heated to  $170^\circ$  with silver sulphate parathioformaldehyde is changed to trioxymethylene.

2. **Acetaldehyde**,  $\text{C}_2\text{H}_4\text{O} = \text{CH}_3.\text{CHO}$ , is formed according to the methods described above, but is generally prepared by the oxidation of ethyl alcohol with potassium bichromate and dilute sulphuric acid. Commercial aldehyde, and especially that employed in the preparation of aniline colors, is obtained from the first runnings in the rectification of spirit. It is made, too, in the oxidation of alcohol in running over wood charcoal. Its production from vinylsulphuric acid,  $\text{SO}_4\text{H}(\text{C}_2\text{H}_3)$ , by boiling with water, is of theoretical interest. (Compare p. 103.)

*Preparation.*—Pour 12 parts  $\text{H}_2\text{O}$  over 3 parts  $\text{K}_2\text{Cr}_2\text{O}_7$ , and then gradually add, taking care to have the solution cooled, a mixture of 4 parts concentrated  $\text{H}_2\text{SO}_4$ , and 3 parts alcohol (90 per cent.); the heat of a water-bath is now applied, and the vapors that escape are condensed in a receiver. The resulting distillate, which consists of alcohol, aldehyde and acetal, is next heated to  $50^\circ$ , and the escaping aldehyde vapors conducted into ether, and this solution saturated with dry  $\text{NH}_3$ , when the aldehyde-ammonia,  $\text{C}_2\text{H}_4\text{O}.\text{NH}_3$ , will separate in a crystalline form. Pure aldehyde may be obtained from this by distilling it together with dilute sulphuric acid. The aldehyde vapors are freed from moisture by conducting them over heated calcium chloride.

Acetaldehyde is a mobile, peculiar-smelling liquid. It boils at  $20.8^\circ$ , and has a sp. gr. of 0.8009 at  $0^\circ$ . It is miscible in all proportions with water, ether and alcohol. It slowly oxidizes when



exposed to air or to acetic acid. From an ammoniacal silver solution it immediately throws out metallic silver as a mirror-like deposit. Nascent hydrogen transforms aldehyde into ethyl alcohol.  $\text{PCl}_5$  and  $\text{PBr}_5$  convert it into  $\text{CH}_3\text{.CHCl}_2$  and  $\text{CH}_3\text{.CHBr}$  (p. 71).

**Ethylaldoxim**,  $\text{CH}_3\text{.CH:N.OH}$ , isonitrosoethane, produced by the action of hydroxylamine upon acetaldehyde (p. 152), boils at  $115^\circ$ , possesses an aldehyde-like odor, and is miscible with water, alcohol and ether.

When an ethereal solution of aldehyde is saturated with dry ammonia, aldehyde-ammonia (ethidene hydramine),  $\text{C}_2\text{H}_4\text{O.NH}_3$  (p. 151), separates out. This compound is readily soluble in water, but not so easily in alcohol, and crystallizes in large, glistening rhombohedra, which fuse at  $70^\circ\text{--}80^\circ$ , and vaporize undecomposed.

On shaking aldehyde with aqueous solutions of acid alkaline sulphites, crystalline compounds, *e. g.*,  $\text{CH}_3\text{.CHO.HSO}_3\text{K}$  (see p. 151), separate. If these be heated together with acids, they break up into their components.

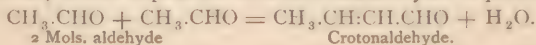
With anhydrous hydrocyanic acid, aldehyde yields  $\text{CH}_3\text{.CH(OH)CN}$  (see p. 151), a liquid readily soluble in water and alcohol, and boiling with slight decomposition at  $183^\circ$ . The alkalis break it up into its components, and concentrated hydrochloric acid converts it into lactic acid.

**Polymeric Aldehydes.** Small quantities of acids ( $\text{HCl}$ ,  $\text{SO}_2$ ) or salts (especially  $\text{ZnCl}_2$ ) convert aldehyde at ordinary temperatures into **paraldehyde**,  $(\text{C}_2\text{H}_4\text{O})_3$ , (see p. 152); the change (accompanied by evolution of heat and contraction) is particularly rapid, if a few drops of sulphuric acid be added to the aldehyde. Paraldehyde is a colorless liquid boiling at  $124^\circ$ , and of sp. gr. 0.9943 at  $20^\circ$ . It dissolves in about 12 vols.  $\text{H}_2\text{O}$ , and is, indeed, more soluble in the cold than in the warm liquid. This behavior would point to the formation of an hydrate. The vapor density agrees with the formula  $\text{C}_6\text{H}_{12}\text{O}_3$ . When distilled with sulphuric acid, ordinary aldehyde is generated.

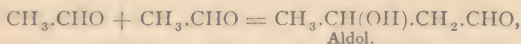
**Metalddehyde**,  $(\text{C}_2\text{H}_4\text{O})_n$ , is produced by the same reagents (see above) acting on ordinary aldehyde at temperatures below  $0^\circ$ . It is a white crystalline body, insoluble in water, but readily dissolved by hot alcohol and ether. If heated to  $112^\circ\text{--}115^\circ$  it sublimes without previously melting, and passes into ordinary aldehyde with only slight decomposition. When heated in a sealed tube the change is complete.

There are many reagents that change meta- and paraldehydes to ordinary aldehyde and its derivatives; *e. g.*,  $\text{PCl}_5$  converts them into ethidene dichloride,  $\text{CH}_3\text{.CHCl}_2$ . They do not combine with  $\text{NH}_3$  or alkaline bisulphites, do not reduce silver solutions, nor do they give aldoxim with hydroxylamine (p. 152). Paraldehyde is not attacked by sodium, even when assisted by heat. These facts go to prove that in the polymeric aldehydes, the aldehyde radicals are linked by oxygen atoms (see p. 152), the same as the alkyls in the ethers. Their refractive power and their specific volume would also indicate that the oxygen atoms present in them are united to carbon by but one affinity.

**Condensation Products.** When acetaldehyde is heated with zinc chloride, water separates and crotonaldehyde is produced:—



Upon protracted contact with dilute sulphuric acid, aldehyde first becomes the so-called aldol (see this):—



which, when heated with zinc chloride, gives up water and also passes into crotonaldehyde:—

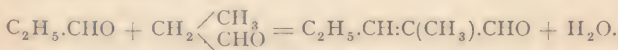


When chlorine is conducted into cold aldehyde chlor-crotonaldehyde,  $\text{CH}_3\cdot\text{CH}:\text{CCl}_2\cdot\text{CHO}$ , and trichlorobutyraldehyde,  $\text{C}_4\text{H}_5\text{Cl}_3\text{O}$  (p. 157), are formed, and by the action of nascent hydrogen (sodium amalgam) there results butylene glycol,  $\text{CH}_3\cdot\text{CH}\cdot\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ .

Sulphuric acid, sodium acetate (*Berichte*, 16, 786), and alkalis (sodium hydrate and baryta water), exert the same power of condensation as zinc chloride and hydrochloric acid.

Such a union of two or more molecules by the linking of carbon atoms (followed either with or without water separation), and the formation of complicated carbon chains is ordinarily termed *condensation*, distinction being made at the same time between the *aldol condensation* and genuine *aldehyde condensation*, in which an exit of water does occur.

In the case of the higher aldehydes (also ketones), the condensation is so made that the oxygen of aldehyde unites with the hydrogen of a  $\text{CH}_2$  group. Thus, from propylaldehyde we get methyl-ethyl acrolein:—



The aldehydes act in a perfectly similar manner upon the esters of malonic acid,  $\text{CH}_2(\text{CO}_2\text{R})_2$ , acetic acid and analogous compounds (*Annalen*, 218, 121).

Another very remarkable condensation is sustained by the aldehydes through the action of ammonia (heating of aldehyde-ammonias); nitrogenous bases (pyridine bases) are produced (p. 157).

*Substituted Aldehydes.* These are obtained by the action of chlorine upon acetaldehyde or ethyl alcohol, the latter being simultaneously oxidized to aldehyde. The only pure compound that can be formed in this manner is the final chlorination product, *trichloraldehyde*.

**Monochloraldehyde**,  $\text{CH}_2\text{Cl}\cdot\text{CHO}$ , is obtained pure by distilling monochloroacetal,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{O}\cdot\text{C}_2\text{H}_5)_2$ , with anhydrous oxalic acid. It is a liquid that boils at  $85^\circ$ , and polymerizes very rapidly to a white mass (*Berichte*, 15, 2245). When oxidized it yields monochloroacetic acid; with  $\text{CNH}$  and hydrochloric acid it becomes  $\beta$ -chlorolactic acid.

**Dichloraldehyde**,  $\text{CHCl}_2\cdot\text{CHO}$ , is produced in the distillation of dichloroacetal,  $\text{CHCl}_2\cdot\text{CH}(\text{O}\cdot\text{C}_2\text{H}_5)_2$ , with concentrated sulphuric acid. It boils at  $88^\circ$ – $90^\circ$ , and when preserved, changes into a solid polymeric modification. The hy-

drate,  $\text{CHCl}_2\cdot\text{CHO} + \text{H}_2\text{O}$ , corresponding to chloral hydrate, fuses at  $43^\circ$ . When it is oxidized with  $\text{HNO}_3$  dichloraldehyde is converted into dichloroacetic acid. It yields dichlorolactic acid by the action of  $\text{CNH}$  and hydrochloric acid.

**Trichloroacetaldehyde**,  $\text{CCl}_3\cdot\text{CHO}$ , **Chloral**, is best prepared by conducting chlorine into alcohol and distilling the crystalline product with sulphuric acid. It is an oily, pungent-smelling liquid, which boils at  $97^\circ$ , and has the sp. gr. 1.541 at  $0^\circ$ . With  $\text{NH}_3$ ,  $\text{CNH}$ , acid sulphites of the alkali metals, etc., chloral furnishes compounds similar to those of ordinary aldehyde; it also reduces an ammoniacal silver solution. When kept for some time it passes into a solid polymeride. It affords trichloroacetic acid when oxidized by  $\text{HNO}_3$ . When heated with alkalis it breaks up into chloroform and a formate:—



When it combines with a small quantity of water chloral changes to

**Chloral Hydrate**,  $\text{C}_2\text{HCl}_3\text{O}\cdot\text{H}_2\text{O} = \text{CCl}_3\cdot\text{CH} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{OH} \end{smallmatrix}$ , which consists of large monoclinic prisms, fusing at  $57^\circ$  and distilling at  $96\text{--}98^\circ$ . The vapors dissociate into chloral and water. Chloral hydrate dissolves readily in water, possesses a peculiar odor and a sharp, biting taste, and, when taken internally, produces sleep. Concentrated sulphuric acid decomposes the hydrate again into water and chloral.

Chloral and alcohol combine to **Chloral Alcoholate**,—trichlorethidene ethyl ether— $\text{CCl}_3\cdot\text{CH} \begin{smallmatrix} \diagup \text{O}\cdot\text{C}_2\text{H}_5 \\ \diagdown \text{OH} \end{smallmatrix}$ , a crystalline solid, fusing at  $56^\circ$  and boiling at  $114\text{--}115^\circ$ . When acetyl chloride is allowed to act upon the preceding derivative the acetyl ester, trichlorethidene ethyl acetin, is produced. This boils at  $198^\circ$ . Concentrated sulphuric acid reproduces chloral from the alcoholate.

Acetic anhydride and chloral yield trichlorethidene diacetate,  $\text{CCl}_3\cdot\text{CH}(\text{O}\cdot\text{C}_2\text{H}_3\text{O})_2$ , which boils at  $221^\circ$ . It unites with ammonia to form **chloral-ammonia**,—trichlorethidene hydramine— $\text{CCl}_3\cdot\text{CH} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{NH}_2 \end{smallmatrix}$ , melting at  $63^\circ$ . With prussic acid it furnishes **chloral-cyanhydrate**,  $\text{CCl}_3\cdot\text{CH} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{CN} \end{smallmatrix}$ , a crystalline derivative, fusing at  $61\text{--}62^\circ$ , and passing into trichlorolactic acid when treated with hydrochloric acid.

**Dibromacetaldehyde**,  $\text{CIBr}_2\cdot\text{CHO}$ , obtained by the bromination of aldehyde or paraldehyde, is a liquid, boiling at  $142^\circ$ . After standing some time it becomes solid—a polymeric modification. It affords a crystalline **hydrate** with water. It combines with  $\text{CNH}$  to form the compound,  $\text{CIBr}_2\cdot\text{CH} \begin{smallmatrix} \diagup \text{CN} \\ \diagdown \text{OH} \end{smallmatrix}$ , from which dibromolactic acid may be obtained.

**Tribromaldehyde**,  $\text{CBr}_3\cdot\text{CHO}$ , **Bromal**, is perfectly analogous to chloral. It boils at  $172\text{--}173^\circ$ , and forms, with water, a solid hydrate which fuses at  $53^\circ$ . The **alcoholate** melts at  $44^\circ$  and decomposes at  $100^\circ$ . Heated with alkalis

bromal breaks up into bromoform and a formate. It yields a cyanide,  $\text{CBr}_3 \cdot \text{CH} \begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix}$ , with  $\text{CNH}$  and this hydrochloric acid converts into tribromolactic acid.

**Sulphur Compounds.**—On passing hydrogen sulphide into an aqueous solution of aldehyde there arises a disagreeable-smelling oil—a compound of thioaldehyde with aldehyde. Two isomeric **trithioaldehydes**,  $(\text{C}_2\text{H}_4\text{S})_3$ , (Ber. 11, 2205), have been obtained from it.

**Thialdin**,  $\text{C}_6\text{H}_{13}\text{NS}_2$ , separates on conducting  $\text{H}_2\text{S}$  into an aqueous solution of aldehyde-ammonia. It consists of large, colorless crystals, fusing at  $43^\circ$ . It shows a neutral reaction, and forms salts with acids.

3. **Propionic Aldehyde**,  $\text{C}_3\text{H}_6\text{O} = \text{C}_2\text{H}_5 \cdot \text{CHO}$ , is obtained from normal propyl alcohol and by the dry distillation of calcium propionate and formate. It is very similar to acetaldehyde, boils at  $49^\circ$ , and has a sp. gr. 0.8066 at  $20^\circ$ . It is soluble in 5 vols.  $\text{H}_2\text{O}$  at  $20^\circ$ . With  $\text{PCl}_5$  it yields  $\text{C}_2\text{H}_5 \cdot \text{CHCl}_2$ .

**Propyl Aldoxim**,  $\text{C}_2\text{H}_5 \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$  (see p. 152), boils at  $131^\circ$ .

**$\beta$ -Chlorpropionic Aldehyde**,  $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CHO}$ . This is produced when  $\text{HCl}$  is added to acrolein; it fuses at  $35^\circ$ , and, when distilled, again breaks up into acrolein and  $\text{HCl}$ . Nitric acid oxidizes it to  $\beta$ -chlorpropionic acid.

4. **Butyraldehydes**,  $\text{C}_4\text{H}_8\text{O} = \text{C}_3\text{H}_7 \cdot \text{CHO}$ . Two isomeric aldehydes of this form exist; they correspond to the two primary butyl alcohols.

(1) **Normal Butyraldehyde**,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$ , from normal butyl alcohol and normal butyric acid, is a liquid boiling near  $75^\circ$ , and has a sp. gr. 0.8170 at  $20^\circ$ . It dissolves in 27 parts  $\text{H}_2\text{O}$ , and oxidizes readily to butyric acid. Heated with alcoholic ammonia it yields the base **paraconine**,  $\text{C}_8\text{H}_{15}\text{N}$ , boiling at  $170^\circ$  and very similar to **conine**,  $\text{C}_8\text{H}_{17}\text{N}$ . The isomeric paraconine obtained from isobutyraldehyde boils at  $146^\circ$ .

**$\beta$ -Chlorbutyraldehyde**,  $\text{CH}_3 \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{CHO}$ , is produced from crotonaldehyde,  $\text{CH}_3 \cdot \text{CH} \cdot \text{CH} \cdot \text{CHO}$ , by the addition of  $\text{HCl}$ , and consists of needles, fusing at  $99^\circ$ . Nitric acid oxidizes it to  $\beta$ -chlorbutyric acid.

**Trichlorbutyraldehyde**,  $\text{CH}_3 \cdot \text{CHCl} \cdot \text{CCl}_2 \cdot \text{CHO}$ , formerly obtained from crotonaldehyde,  $\text{C}_4\text{H}_3\text{Cl}_3\text{O}$ , is produced by the action of chlorine upon acetaldehyde or paraldehyde, the first product being chlorcrotonaldehyde,  $\text{CH}_3 \cdot \text{CH} \cdot \text{CCl} \cdot \text{COH}$  (p. 159), which further unites with  $\text{Cl}_2$ , yielding the so-called butyl-chloral (*Annalen*, 219, 374). The latter compound, like the ordinary chloral, is a heavy, oily liquid, boiling at  $163$ – $165^\circ$ , and forming with water the hydrate,  $\text{C}_4\text{H}_5\text{Cl}_3\text{O} + \text{H}_2\text{O}$ ; this last crystallizes in tablets, fusing at  $78^\circ$ . The alkalis decompose butyl chloral into acetic acid, potassium chloride and allylene dichloride,  $\text{CH}_3 \cdot \text{CCl} \cdot \text{CHCl}$ . It yields a trichlorbutyric acid when oxidized with nitric acid.

(2) **Isobutyraldehyde**,  $(\text{CH}_3)_2\text{CH} \cdot \text{CHO}$ , obtained from fermentation butyl alcohol and calcium isobutyrate, has the sp. gr. 0.7898 at  $20^\circ$  and boils at  $63^\circ$ . It dissolves in nine volumes of water at  $20^\circ$ . A small quantity of concentrated sulphuric acid



converts it into **Para-isobutyraldehyde**,  $(C_4H_8O)_3$ , which crystallizes in brilliant needles, melting at  $60^\circ$ , and boiling at  $194^\circ$ .

5. **Amyl Aldehydes**,  $C_5H_{10}O = C_4H_9 \cdot CHO$ , **Valeraldehydes**. There are four possible isomerides; two of these are known:—

**Normal Amyl Aldehyde**,  $(CH_3)_2(CH_2)_3CHO$ , from valeric acid, boils at  $102^\circ$ . **Isoamyl Aldehyde**,  $(CH_3)_2CH \cdot CH_2 \cdot CHO$ , from the amyl alcohol of fermentation and from isovaleric acid, is a liquid, with fruit-like odor, boiling at  $92^\circ$ , and polymerizing readily. When oxidized it becomes isovaleric acid. On heating with alcoholic ammonia to  $150^\circ$  it yields two basic compounds, *valeridine*,  $C_{10}H_9N$ , and *valeritrine*,  $C_{15}H_{27}N$ , which boils near  $250^\circ$ .

**Normal Hexyl Aldehyde**,  $C_6H_{12}O = C_5H_{11} \cdot CHO$ , **Caproyl Aldehyde**, from caproic acid, boils at  $128^\circ$ . **Normal Heptyl Aldehyde**,  $C_7H_{14}O$ , **œnanthyl aldehyde**, or **œnanthol**, is produced along with hendecatoic acid in the distillation of castor-oil, best under diminished pressure. It is a pungent-smelling liquid, boiling at  $153\text{--}154^\circ$ . It becomes normal heptylic acid,  $C_7H_{14}O_2$ , when oxidized with dilute nitric acid (1 : 2 vols.  $H_2O$ ).

The higher aldehydes are most advantageously prepared by the distillation, under diminished pressure, of the barium salts of the corresponding fatty acids with barium formate (*Ber.*, 16, 1716). Like their acids, they all have normal structure. They can be boiled without decomposition only under a somewhat diminished pressure.

**Decatoic Aldehyde**,  $C_{10}H_{20}O$ , **Capric Aldehyde**, obtained from capric acid, boils at  $106^\circ$  under a pressure of 15 mm.

**Dodecattylic Aldehyde**,  $C_{12}H_{24}O$ , **Lauric Aldehyde**, from lauric acid, crystallizes in shining tablets, fusing at  $44.5^\circ$ , and boiling at  $142^\circ$  (22 mm.).

**Tetradecattylic Aldehyde**,  $C_{14}H_{28}O$ , **Myrisitaldehyde**, made from myristic acid, melts at  $52.5^\circ$ , and under 22 mm. pressure boils at  $168^\circ C$ .

**Hecdecattylic Aldehyde**,  $C_{16}H_{32}O$ , **Palmitic Aldehyde**, from palmitic acid, fuses at  $58.5^\circ$ , and under 22 mm. pressure boils at  $192^\circ C$ .

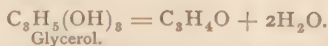
**Octdecattylic Aldehyde**,  $C_{18}H_{36}O$ , **Stearaldehyde**, consists of tablets having a bluish lustre. It fuses at  $63.5^\circ$ , and boils at  $192^\circ C$ . (under 22 mm. pressure).

## 2. UNSATURATED ALDEHYDES, $C_n H_{2n-2}O$ .

These derivatives bear the same relation to the alcohols of the allyl series as do the aldehydes just considered to the alcohols  $C_n H_{2n+2}O$ , of the saturated hydrocarbons. Inasmuch as they are unsaturated compounds they are capable of directly saturating two affinities.

The first and lowest member of the series is:—

**Acrylaldehyde**,  $C_3H_4O = CH_2 \cdot CH \cdot CHO$ , or **Acroleïn**. This is produced by the oxidation of allyl alcohol and by the distillation of glycerol or fats:—



One part of glycerol is distilled with two parts of acid potassium sulphate. The distillate is redistilled over lead oxide (*Ann. Suppl.*, 3, 180).

Acroleïn is a colorless, mobile liquid, boiling at  $52^\circ$ , and possessing a sp. gr. of 0.8410 at  $20^\circ$ . It has a pungent odor and attacks the mucous membranes in a frightful manner. The odor of burning fat is occasioned by acroleïn. It is soluble in 2–3 parts water.

It reduces an ammoniacal silver solution, with formation of a mirror-like deposit, and when exposed to the air it oxidizes to acrylic acid. It does not combine with primary alkaline sulphites. Nascent hydrogen converts it into allyl alcohol.

Phosphorus pentachloride converts acrolein into propylene dichloride,  $\text{CH}_2:\text{CH}.\text{CHCl}_2$ , boiling at  $84^\circ \text{C}$ . With hydrochloric acid it yields  $\beta$ -chlorpropionic aldehyde (p. 157). With bromine it affords a dibromide,  $\text{CH}_2.\text{Br}.\text{CHBr}.\text{CHO}$ , which when oxidized becomes  $\beta$ -dibromopropionic acid.

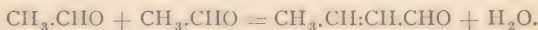
When preserved, acrolein passes into an amorphous, white mass (*disacryl*). On warming the  $\text{HCl}$  compound of acrolein (see above) with alkalis or potassium carbonate *metacrolein* is obtained. The vapor density of this agrees with the formula  $(\text{C}_3\text{H}_4\text{O})_3$ . It crystallizes from alcohol in tablets, fusing at  $45-46^\circ$ , and dissociating at  $160^\circ \text{C}$ .

Ammonia changes acrolein to the so-called *acrolein-ammonia*,  $\text{C}_6\text{H}_9\text{NO} + \frac{1}{2}\text{H}_2\text{O}$  :—



This is a yellowish mass that on drying becomes brown, and forms amorphous salts with acids. It yields *picoline*,  $\text{C}_6\text{H}_7\text{N}$  (methyl-pyridine,  $\text{C}_5\text{H}_4\text{N}.\text{CH}_3$ ), when distilled.

**Crotonaldehyde**,  $\text{C}_4\text{H}_6\text{O} = \text{CH}_3.\text{CH}:\text{CH}.\text{CHO}$ , is obtained by the condensation of acetaldehyde (p. 154) when heated with dilute hydrochloric acid, with water and zinc chloride, or with a sodium acetate solution, to  $100^\circ \text{C}$ . (*Ber.*, 14, 514 and 516):—



It is also produced when the sulphuric acid solution of bromethylene is boiled with water (see p. 103). Crotonaldehyde is a liquid with irritating odor, soluble in water; at  $0^\circ$  it has a sp. gr. of 1.033, and boils at  $104-105^\circ$ . On exposure to the air it oxidizes to crotonic acid, and it also reduces silver oxide. It combines with hydrochloric acid to form  $\beta$ -chlorbutyraldehyde (p. 157); on standing with hydrochloric acid it unites with water and becomes aldol. Iron and acetic acid change it to croton alcohol, butyraldehyde and butyl alcohol.

**$\alpha$ -Chlorcrotonaldehyde**,  $\text{CH}_3.\text{CH}:\text{CCl}.\text{CHO}$ , is a by-product in the preparation of butyl-chloral, and may also be obtained by the condensation of aldehyde with monochloraldehyde. It is a pungent-smelling oil, boiling at  $150^\circ$ . It combines directly with two atoms of chlorine to butyl chloral (p. 157).

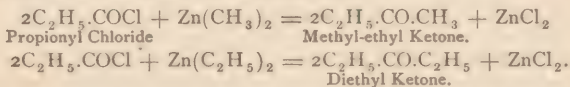
When the alcoholic solution of acetaldehyde-ammonia is heated to  $120^\circ$ , **Crotonal-ammonia**,  $\text{C}_8\text{H}_{13}\text{NO}$  (*Oxtetraldine*), is produced. This bears the same relation to crotonaldehyde that acrolein-ammonia does to acrolein. It is a brown amorphous mass, yielding amorphous salts with acids. When heated it breaks up into water and **collidine**,  $\text{C}_8\text{H}_{11}\text{N} = \text{trimethylpyridine}$ ,  $\text{C}_5\text{H}_2\text{N}(\text{CH}_3)_3$ .

**Methyl-ethyl Acrolein**,  $\text{C}_2\text{H}_5.\text{CH}:\text{C}(\text{CH}_3).\text{CHO}$ , is produced by the condensation of propionic aldehyde (p. 157), and boils at  $137^\circ \text{C}$ .

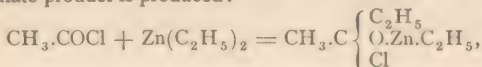
## KETONES.

The ketones are characterized by the group CO in combination with two alkyls. They share many analogies with the aldehydes, indicated by the similar methods of production (see p. 148). We have the following specific methods for their formation:—

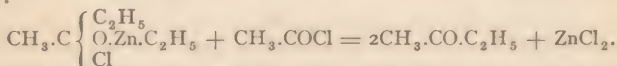
1. The action of the zinc alkyls (1 molecule) upon the chlorides of the acid radicals (2 molecules):—



To the zinc alkyl (1 molecule), cooled by ice, there are added drop by drop at first, then rapidly, 2 molecules of the acid chloride and the product of the reaction is immediately decomposed by a large quantity of water. The reaction is similar to that occurring in the formation of the tertiary alcohols (p. 90). At first the same intermediate product is produced:

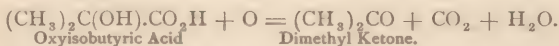


which, (with a second molecule of the acid chloride) afterwards yields the ketone:—

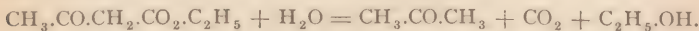


In many cases, especially in the preparation of the pinacolines, it is, however, more advantageous to employ double the quantity of the zinc alkyl (1 molecule to 1 molecule acid chloride) which will serve to dilute the mixture (*Ann.* 188, 144); in this manner the intermediate product forms the ketone with water, and there occurs a simultaneous evolution of paraffins. The aqueous solution is distilled, and the ketone separated from it by means of soda.

2. The oxidation of the acids of the lactic series with secondary alkyls, by means of bichromate of potash and dilute sulphuric acid (see p. 149):—



3. The decomposition of the aceto-acetic acids and their esters (see these):—

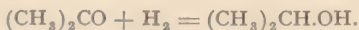


The ketones are also produced in the dry distillation of wood, sugar, and many other carbon compounds.

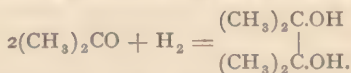
The ketones are generally ethereal-smelling, volatile liquids, insoluble in water. They do not reduce ammoniacal silver solutions. They combine, like aldehydes, with the primary alkaline sulphites; but it appears that of the higher ketones only those are adapted to

this reaction in which the group CO is in combination with the methyl group. Boiling alkaline carbonates again separate the ketone from these compounds (p. 149). Hence, these reactions serve both for the isolation and the purification of these derivatives.

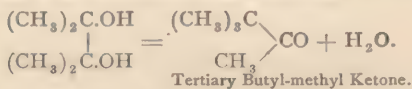
Nascent hydrogen (sodium amalgam) converts them into secondary alcohols :—



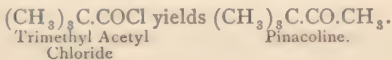
At the same time there occurs here, as with the aldehydes (p. 154), a condensation of the ketone molecule, accompanied by the formation of dihydric alcohols:



These are termed *pinacones*. When heated with acids they sustain a peculiar transposition of atoms, and are converted into ketones :—

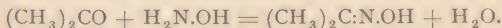


Ketones like these, containing a tertiary alkyl group, are designated *pinacolines*. They may be synthesized by the action of zinc alkyls upon the chlorides of such fatty acids as contain tertiary alkyls :—



The ketones also unite with HCN, forming oxycyanides, *e. g.*,  $(\text{CH}_3)_2\text{C}(\text{OH}).\text{CN}$  (see *Berichte*, 15, 2306), from which the corresponding oxyacids may be obtained (see p. 151). Similarly, acetone in the presence of caustic soda combines with chloroform, yielding *acetone chloroform*,  $(\text{CH}_3)_2\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{CCl}_3 \end{array}$ . This, too, can be converted into the corresponding oxyacid (*Berichte*, 15, 2305).

All the ketones (like the aldehydes, p. 152), combine with hydroxylamine, and become oximid- or isonitroso-compounds, called *acetoxims* (see p. 163):—

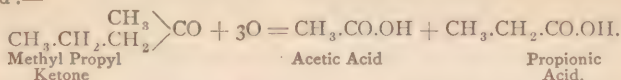


All bodies possessing the ketone group CO (or the aldehyde group), *e. g.*, the ketonic acids and alcohols, react with hydroxylamine in a manner similar to that of the ketones. Some acid anhydrides, *e. g.*, phthalic anhydride (*Berichte*, 16, 1780), do the same. This is not, however, the case with the lactones and alkyl oxides. The diketones, such as glyoxal,  $\text{ClHO.CHO}$ , are capable of a double reaction with hydroxylamine, yielding compounds known as *acetoximic acids* or *glyoxims* (see p. 164, and *Berichte*, 16, 506). The ketones react more readily with the hydrazines, forming crystalline compounds, than with hydroxylamine (*Berichte*, 16, 661, 17, 576).

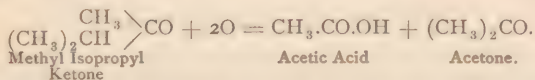
The ketones cannot be directly oxidized. When they are boiled with  $\text{K}_2\text{Cr}_2\text{O}_7$  and dilute sulphuric acid, they break up in such a manner that the CO group passes out in combination with the lower alkyl, thus producing an acid. Should



the other higher alkyl chance to be of a primary character, it, too, is oxidized to an acid :—

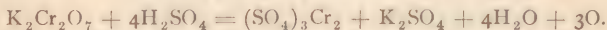


When the higher radical is secondary, it first becomes a ketone, and this decomposes further :—



When the CO group is united to carbon atoms carrying an equal number of hydrogen atoms, it remains with the higher alkyl when decomposition occurs (*Berichte*, 15, 1194).

To oxidize ketones, proceed as follows: dilute a mixture consisting of 1 molecule ketone, 1 molecule  $\text{K}_2\text{Cr}_2\text{O}_7$  and 4 molecules  $\text{H}_2\text{SO}_4$ , with 5–10 parts water, and heat the same in a large flask, provided with a long, upright glass tube serving as a condenser. The reaction is complete when the mixture assumes the pure, green color of chromium sulphate (compare *Annalen*, 190, 349) :—



The acids produced are distilled over with water.

A similar decomposition is sustained by the ketones when oxidized by free chromic acid, potassium permanganate,  $\text{PbO}_2$ , etc. (*Annalen*, 186, 257.)

**Dimethyl Ketone**,  $\text{C}_3\text{H}_6\text{O} = (\text{CH}_3)_2\text{CO}$ , **Acetone**. In addition to the general methods of formation, acetone is produced by heating chlor- and brom-acetol (p. 74) with water to  $160^\circ$ – $180^\circ$  :—



and also by the dry distillation of tartaric and citric acids, sugar, wood, etc. This accounts for its presence in crude wood spirit (p. 94). It is usually obtained by the dry distillation of calcium acetate (p. 149).

Of theoretical interest is its formation from  $\beta$ -chlor- and brom-propylene,  $\text{CH}_3\text{.CHBr.CH}_2$ , when these are heated with water to  $200^\circ$ , or dissolved in sulphuric acid and boiled with water. We would naturally expect an alcohol  $\text{CH}_3\text{.C(OH).CH}_2$  to be formed here, but a transposition of atoms occurs and acetone results (see p. 103). Acetone is similarly formed from allylene,  $\text{CH}_3\text{.C:CH}$ , by action of sulphuric acid or  $\text{HgBr}_2$  in the presence of water (p. 61).

Acetone is a mobile, peculiar-smelling liquid, boiling at  $56.5^\circ$  and having a sp. gr. of 0.7920 at  $20^\circ$ . It is miscible with water, alcohol and ether. Calcium chloride or other salts set it free from its aqueous solution. The compound it forms with primary sodium sulphite has one molecule of water, and consists of pearly scales, easily soluble in water. Excess of sodium sulphite or alcohol separates it from its solution. When in aqueous solution, sodium amalgam converts it into isopropyl alcohol. The chromic acid mixture

oxidizes it to acetic and formic acids, which, as a general thing, are still further oxidized to  $\text{CO}_2$  and water:—



The ketones are similarly decomposed when their vapors are conducted over heated soda-lime.

An aqueous acetone solution, mixed with KOH and an iodine solution, yields iodoform (p. 75). This reaction serves to detect acetone even in presence of alcohol (*Berichte*, 13, 1004). All ketones containing the group  $\text{CO}\cdot\text{CH}_3$ , do the same (*Berichte*, 14, 1948).  $\text{PCl}_5$  and  $\text{PBr}_5$  convert acetone into chlor- and brom-acetol (p. 73).

### ACETONE SUBSTITUTION PRODUCTS.

These result by the direct action of chlorine or bromine upon acetone and by various other methods.

**Monochloracetone**,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , is obtained by conducting chlorine into cold acetone, or by the action of hypochlorous acid upon monochlor- or monobrom-propylene:—



It is a liquid, insoluble in water; its vapors provoke tears. **Monobromacetone**,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ , decomposes upon distillation.

There are two possible **Dichloracetones**,  $\text{C}_3\text{H}_4\text{Cl}_2\text{O}$ : ( $\alpha$ )  $\text{CH}_3\cdot\text{CO}\cdot\text{CHCl}_2$  and ( $\beta$ )  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ . The first is formed on treating warmed acetone with chlorine, and is obtained from dichloroaceto-acetic ester, on boiling the same with hydrochloric acid. (*Berichte*, 15, 1164). It is an oily liquid, with a sp. gr. of 1.236 at  $21^\circ$ , and boils at  $120^\circ$ . The  $\beta$ -dichloroacetone is produced in the oxidation of dichlorhydrin,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$  (see glycerol), with potassium dichromate and sulphuric acid (*Berichte*, 13, 1701). It consists of rhombic plates, fusing at  $45^\circ$ , and boiling at  $172^\circ$ – $174^\circ$ . Bromine affords similar substitution products.

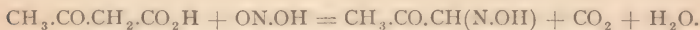
$\beta$ -**Di-iodoacetone**,  $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{CH}_2\text{I}$ , forms when iodine chloride acts upon acetone. It fuses at  $62^\circ$  and decomposes about  $120^\circ$ .

**Hydroxylamine- or Oximido-Derivatives** (p. 78 and p. 161). **Acetoxim**,  $(\text{CH}_3)_2\text{C}:\text{N}\cdot\text{OH}$ , dimethylacetoxim, formed in the action of hydroxylamine upon acetone (p. 161), is a compound readily soluble in water, alcohol and ether. It fuses at  $60^\circ$  and boils at  $135^\circ$ . Boiling acids regenerate acetone and hydroxylamine.

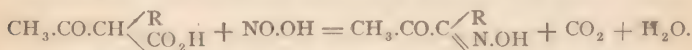
The hydroxyl group present in this compound may be replaced by acid radicals through the agency of acid chlorides or anhydrides. With sodium alcoholate, the sodium derivative results, which yields the alkyl ethers,  $(\text{CH}_3)_2\text{C}:\text{N}\cdot\text{OR}$ , when acted upon by the alkylogens. On boiling these ethers with acids, acetone and alkylized hydroxylamines,  $\text{NH}_2\text{OR}$  (*Berichte*, 16, 170), are produced.

**Isonitroso-acetone**,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}:\text{N}\cdot\text{OH}$ . This is obtained from the isonitroso-aceto-acetic ester (*Berichte*, 15, 1326). Nitrous

acid converts aceto-acetic acid directly into isonitrosoacetone and carbon dioxide :—



The insonitroso-derivatives of the higher acetones are made directly, after the same manner, from monoalkylized aceto-acetic acids and their esters :—

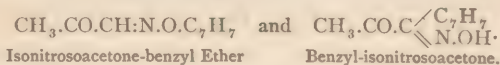


The dialkyl aceto-acetic acids are not reactive (*Berichte*, 15, 3067).

The isonitroso-acetones are colorless, crystalline bodies, readily soluble in alcohol-ether and chloroform; but, as a general thing, they dissolve with difficulty in water. They impart an intense yellow color to their alkaline solutions, and with phenol and sulphuric acid yield a yellow coloration, but not the nitroso-reaction (see p. 79). When boiled with concentrated hydrochloric acid they lose hydroxylamine.

Isonitroso-acetone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{N}\cdot\text{OH})$ , is very readily soluble in water; crystallizes in silvery, glistening tablets or prisms; fuses at  $65^\circ$ , and decomposes at higher temperatures, but may be volatilized in a current of steam.

By the action of sodium alcoholate upon benzylchloride we get the benzyl-ether, which is isomeric with benzyl-isonitroso-acetone, obtained from benzyl-aceto-acetic acid :—



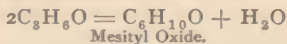
This is proof sufficient of the presence of the oximid group  $\text{N}\cdot\text{OH}$  in the isonitroso-compounds (*Berichte*, 15, 3072). For the salts of the isonitrosoketones consult *Berichte*, 16, 835.

When the isonitroso-acetones are reduced with tin and hydrochloric acid they afford peculiar bases, called *ketines* ( $\text{C}_6\text{H}_8\text{N}_2$ , ketine,  $\text{C}_8\text{H}_{12}\text{N}_2$ , dimethyl ketine); while the  $\alpha$ -isonitroso-acids under the same treatment are reduced to amido-acids (*Berichte*, 15, 3073, and 17, 819).

Any further action of hydroxylamine (or its  $\text{HCl}$  salt, *Berichte*, 16, 182) upon isonitroso-acetone (or upon  $\alpha$ -dichloroacetone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CHCl}_2$ ) leads to a replacement of the ketone oxygen and the formation of

**Acetoximic Acid**,  $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}(\text{N}\cdot\text{OH})$ , or **Methylglyoxim**, a derivative of glyoxim,  $\text{CH}(\text{N}\cdot\text{OH})\cdot\text{CH}(\text{N}\cdot\text{OH})$ , (see p. 161) obtained from glyoxal,  $\text{CHO}\cdot\text{CHO}$ . Similarly the *dialkyl glyoxims*, like  $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}_3$ , dimethylglyoxim, are derived from the higher isonitroso-ketones. The glyoxims are solid, crystalline bodies which dissolve with difficulty in water, and sublime without decomposition. Methyl glyoxim melts at  $153^\circ$ ; methyl-ethyl glyoxim at  $170^\circ$ . Glyoxim and methyl glyoxim show an acid reaction, and dissolve in alkalis without imparting color, because the hydrogen of the  $\text{CH}$ -group is replaced. The dialkyl glyoxims, on the other hand, are insoluble in alkalis and do not yield salts (*Berichte*, 16, 180, 506, and 2185).

**Condensation Products.**—By the action of dehydrating agents ( $\text{H}_2\text{SO}_4$ , burnt lime, zinc chloride, hydrochloric acid) and sodium, acetone (like aldehyde p. 154) loses a molecule of water, and condenses to complex molecules. Mesityl oxide, phorone and mesitylene are produced in this way:—



Mesityl Oxide.



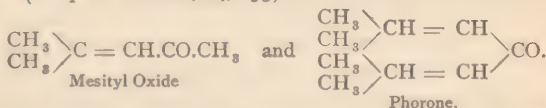
Phorone.

To prepare mesityl oxide and phorone, saturate acetone with  $\text{HCl}$  and let stand for some time, then treat the product with aqueous potash. On diluting with water an oily liquid separates, consisting of mesityl oxide and phorone, which are separated by fractional distillation (*Ann.* 180, 4).

**Mesityl Oxide**,  $\text{C}_6\text{H}_{10}\text{O}$ , is a mobile liquid, smelling like peppermint and boiling at  $130^\circ$ . It acts like acetone; it takes on hydrogen, combines with sodium bisulphite and forms a *chloride*,  $\text{C}_6\text{H}_{10}\text{Cl}_2$ , with  $\text{PCl}_5$ . When boiled with dilute sulphuric or hydrochloric acid mesityl oxide decomposes into two molecules of acetone. It combines directly with  $\text{Br}_2$  and  $\text{HI}$ .

**Phorone**,  $\text{C}_9\text{H}_{14}\text{O}$ , crystallizes in large, yellow prisms, melting at  $28^\circ$  and boiling at  $196^\circ$ . Boiled with dilute sulphuric acid it breaks up into 3 molecules of acetone (mesityl oxide appears as an intermediate product). With bromine it forms a tetrabromide, fusing at  $86^\circ$ .

Acetone condenses to mesityl oxide and phorone in the same manner that acetaldehyde becomes crotonaldehyde (p. 154). Their structure probably agrees with the formulas (compare *Berichte*, 14, 253):—



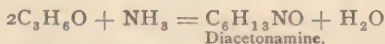
Both mesityl oxide and phorone unite with hydroxylamine, yielding corresponding acetoxims (*Berichte*, 16, 494).

**Mesitylene**,  $\text{C}_9\text{H}_{12}$ , is produced when acetone is distilled with concentrated sulphuric acid:—

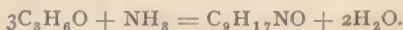


This is a derivative of benzene (see this). It is also produced from mesityl oxide and phorone, through the action of sulphuric acid, but if phorone be heated with  $\text{P}_2\text{O}_5$ , pseudo-cumene is obtained. Other ketones, when acted upon with sulphuric acid, also afford analogous benzene derivatives.

**Acetone Bases.**—When ammonia acts on acetone a condensation of two and three molecules occurs, giving rise to the bases: **Diacetonamine** and **Triacetoneamine**:—



Diacetonamine.



Triacetoneamine.

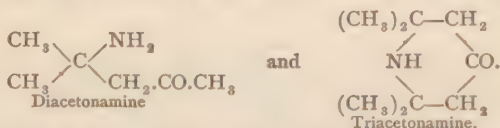
**Diacetonamine** is a colorless liquid, not very soluble in water. When distilled it decomposes into mesityl oxide and  $\text{NH}_3$ ; conversely mesityl oxide and  $\text{NH}_3$  combine to form diacetoneamine. It acts strongly alkaline and is an amide base, forming crystalline salts with one equivalent of acid. If potassium nitrite



be allowed to act on the  $\text{HCl}$ -salt *diacetone alcohol*,  $(\text{CH}_3)_2\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ , results; this loses water and becomes mesityl oxide.

**Triacetoneamine** crystallizes in anhydrous needles, melting at  $39.6^\circ$ . With one molecule of water it forms large quadratic plates, fusing at  $58^\circ$ . It is an imide base (p. 128) with feeble alkaline reaction; potassium nitrite converts its  $\text{HCl}$  salt into the nitroso-amine compound,  $\text{C}_9\text{H}_{16}(\text{NO})\text{NO}$ , which fuses at  $73^\circ$  and passes into phorone when boiled with caustic soda. Hydrochloric acid regenerates triacetoneamine from the nitroso-derivative.

Diacetoneamine and triacetoneamine are intimately related to mesityl oxide and phorone (p. 165); their structure probably corresponds to the formulas:—



By the oxidation of diacetoneamine with a chromic acid mixture (p. 162) we get amido-isobutyric acid,  $(\text{CH}_3)_2\text{C}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , and amido-isovaleric acid,  $(\text{CH}_3)_2\cdot\text{C}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . By the addition of  $2\text{H}$  to triacetoneamine, converting the  $\text{CO}$  group into  $\text{CH}\cdot\text{OH}$ , there results an *alkamine*,  $\text{C}_9\text{H}_{19}\text{NO}$ , which may be viewed as tetramethyl oxypiperidine. By the abstraction of water from this the base  $\text{C}_9\text{H}_{17}\text{N}$ , triacetoneine, results. This approaches tropidine,  $\text{C}_8\text{H}_{13}\text{N}$ , very closely (*Ber.*, 16, 1604 and 2236).

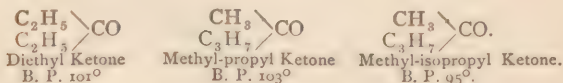
## ACETONE HOMOLOGUES.

**Methyl-ethyl Ketone**,  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array} \text{CO} = \text{C}_4\text{H}_8\text{O}$ , is formed:—

1. By oxidation of secondary butyl alcohol (p. 98).
2. By action of zinc ethide on acetyl chloride or zinc methyl upon propionyl chloride.
3. By distillation of a mixture of calcium propionate and acetate.
4. By oxidation of methyl-ethyl oxyacetic acid and from methyl aceto-acetic ester (see this).

Methyl-ethyl ketone is an agreeably smelling liquid, having a specific gravity of 0.812 at  $13^\circ$ , and boiling at  $81^\circ$ . It combines with the primary sulphites. When oxidized with chromic acid it yields two molecules of acetic acid. Its acetoxim,  $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}_2\text{H}_5$  (p. 163), is liquid and boils at  $153^\circ$ . The isonitroso compound,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}_3$ , *isonitroso-methyl acetone*, crystallizes in pearly tables, melting at  $74^\circ$ , and boiling at  $185^\circ$ . Dimethyl glyoxim,  $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}_3$ , (p. 164) consists of colorless crystals, which melt on rapid heating.

**Ketones**,  $\text{C}_6\text{H}_{10}\text{O}$ :—



These are produced according to the methods generally employed for making the ketones. When boiled with chromic acid they decompose according to the rules of oxidation (p. 161) and also otherwise exhibit all the usual ketone reactions.

*Diethyl Ketone*, called also **Propione**, because obtained by the distillation of calcium propionate, is obtained from carbon monoxide and potassium ethylate (p. 141). It is distinguished from the two methyl propyl ketones by not yielding compounds with the primary alkaline sulphites.

Of the higher ketones may be mentioned :—

**Methyl-tertiary Butyl Ketone**,  $C_6H_{12}O = C_3H_9 \begin{smallmatrix} CH_3 \\ \diagup \end{smallmatrix} CO$ , with the tertiary butyl group  $(CH_3)_3C$ , called **Pinacolone**, is obtained from the hexylene glycol termed pinacone, on warming with hydrochloric or dilute sulphuric acid (p. 161); also by the action of zinc methyl on trimethyl acetyl chloride. It boils at  $160^\circ$ . Its specific gravity at  $0^\circ$  is 0.823. When oxidized with chromic acid it decomposes into acetic and trimethyl acetic acids. Nascent hydrogen converts it into pinacolyl alcohol (p. 101).

**Dipropyl Ketone**,  $C_7H_{14}O = (C_3H_7)_2CO$ , **Butyrone**, is the principal product of the distillation of calcium butyrate. It boils at  $144^\circ$ , and at  $20^\circ$  has a specific gravity equal to 0.8200. A chromic acid mixture changes it to butyric and propionic acids.

**Methyl Hexyl Ketone**,  $C_8H_{16}O = C_6H_{13} \begin{smallmatrix} CH_3 \\ \diagup \end{smallmatrix} CO$ , **Methyl cœnanthol**, is formed by the oxidation of the corresponding octyl alcohol and the distillation of calcium cœnanthylate and acetate. It boils at  $171^\circ$ ; sp. gr. 0.818. It yields acetic and caproic acids when oxidized.

**Methyl-nonyl Ketone**,  $C_{11}H_{22}O = C_9H_{19} \begin{smallmatrix} CH_3 \\ \diagup \end{smallmatrix} CO$ , is the chief constituent of oil of rue (from *Ruta graveolens*); it may be extracted from this by shaking with primary sodium sulphite. It is produced in the distillation of calcium caprate with calcium acetate. It is a bluish, fluorescent oil, which on cooling solidifies to plates, melting at  $+13^\circ$ , and boiling at  $225^\circ$ . When oxidized it yields acetic and pelargonic,  $(C_9H_{18}O_2)$ , acids.

The following additional ketones have been obtained by distilling the barium salts of fatty acids with barium acetate (*Berichte*, 15, 1710):—

$C_{12}H_{24}O = C_{10}H_{21}.CO.CH_3$	from undecylic acid.	Melting Points of the Ketones.	{	21°
$C_{13}H_{26}O = C_{11}H_{23}.CO.CH_3$	“ lauric “			
$C_{14}H_{28}O = C_{12}H_{25}.CO.CH_3$	“ tridecylic “			
$C_{15}H_{30}O = C_{13}H_{27}.CO.CH_3$	“ myristic “			
$C_{16}H_{32}O = C_{14}H_{29}.CO.CH_3$	“ pentadecatoic acid.			
$C_{17}H_{34}O = C_{15}H_{31}.CO.CH_3$	“ palmitic acid.			
$C_{18}H_{36}O = C_{16}H_{33}.CO.CH_3$	“ margaric “			
$C_{19}H_{38}O = C_{17}H_{35}.CO.CH_3$	“ stearic “			
				55.5°

When the salts of the higher fatty acids are distilled alone (p. 149) the simple ketones (with two similar alkyls) result :—

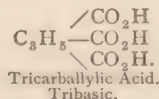
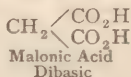
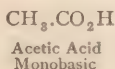
$C_{11}H_{22}O = (C_5H_{11})_2CO$	caprone	from caproic acid.	Melting Points of the Ketones.	{	14.6°
$C_{13}H_{26}O = (C_6H_{13})_2CO$	cœnanthone	“ cœnanthyllic acid.			
$C_{15}H_{30}O = (C_7H_{15})_2CO$	caprylone	“ caprylic “			
$C_{17}H_{34}O = (C_8H_{17})_2CO$	nonone	“ nonoic “			
$C_{23}H_{46}O = (C_{11}H_{23})_2CO$	laurone	“ lauric “			
$C_{27}H_{54}O = (C_{13}H_{27})_2CO$	myristone	“ myristic “			
$C_{31}H_{62}O = (C_{15}H_{31})_2CO$	palmitone	“ palmitic “			
$C_{35}H_{70}O = (C_{17}H_{35})_2CO$	stearone	“ stearic “			
					88°

The corresponding paraffins are obtained when these ketones are reduced (see p. 50).

## MONOBASIC ACIDS.

The organic acids are characterized by the atomic group,  $\text{CO}_2\text{H}$ , called *carboxyl*. The hydrogen of this can be replaced by metals, forming salts (see p. 85). These organic acids may be compared to the analogously constituted sulphonic acids, containing the sulpho-group,  $\text{SO}_2\text{OH}$ .

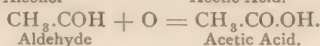
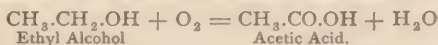
The number of carboxyl groups present in them determines their basicity, and distinguishes them as mono-, di-, tri-basic, etc., or as mono-, di- and tri-carboxylic acids:—



We can view the monobasic *saturated* acids as combinations of the carboxyl group with alcohol radicals; they are ordinarily termed *fatty acids*. The *unsaturated* acids of the acrylic acid and propiolic acid series, corresponding to the unsaturated alcohols, are derived from the fatty acids by the exit of two and four hydrogen atoms.

The most important and general methods of obtaining the monobasic acids are:—

1. Oxidation of the primary alcohols and aldehydes:—



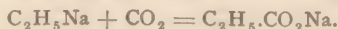
2. The transformation of the cyanides of the alcohol radicals (the so-called nitriles), by heating them with alkalies or dilute mineral acids. The cyanogen group changes to the carboxyl group, while the nitrogen separates as ammonia:—



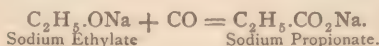
The change of the nitriles to acids is, in many instances, most advantageously executed by digesting the former with sulphuric acid (diluted with an equal volume of water); the fatty acid will then appear as an oil upon the top of the solution. (*Berichte*, 10, 262.)

To convert the nitriles directly into esters of the acids, dissolve them in alcohol, and conduct  $\text{HCl}$  into this solution, or warm the same with sulphuric acid. (*Berichte*, 9, 1590.)

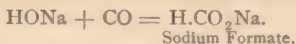
3. Action of carbon dioxide upon sodium alkyls (see p. 141):—



4. Action of carbon monoxide upon the sodium alcoholates heated to  $160^\circ\text{--}200^\circ$ .

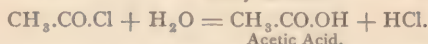
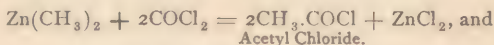


Formic acid results when the caustic alkalies are employed :—

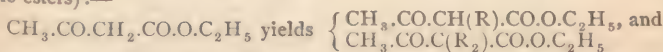


Usually, the reaction is very incomplete, and is often accompanied by secondary reactions, resulting in the formation of higher acids. (*Annalen* 202, 294.)

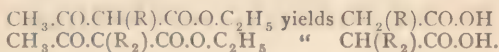
5. By the action of phosgene gas upon the zinc alkyls. At first acid chlorides are formed, but they subsequently yield acids with water :—



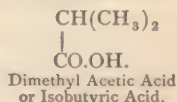
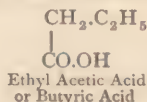
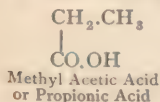
6. The following is a very interesting and a commonly applied method for the synthesis of the fatty acids. By the action of sodium upon acetic esters, the so-called aceto-acetic esters are produced, in which, by the aid of sodium and alkyl iodides, one and two hydrogen atoms can be replaced by alkyls (R) (see aceto-acetic esters) :—



Sodium alcoholate decomposes these alkyllic esters in such a manner, that the group  $\text{CH}_3.\text{CO}$  splits off and the fatty acid esters are produced, but are at once saponified, yielding salts :—

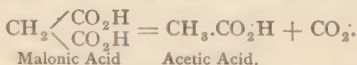


We may regard the acids thus obtained as the direct derivatives of acetic acid,  $\text{CH}_3.\text{CO.OH}$ , in which one and two hydrogen atoms of the  $\text{CH}_3$  group are replaced by alkyls; hence, the designations, methyl and dimethyl acetic acid, etc. :—



Very many fatty acids have been prepared in the above way (first by Frankland and Duppa).

7. From the dicarboxylic acids, in which the two carboxyl groups are in union with the same carbon atom. On the application of heat, these sustain a loss of carbon dioxide :—

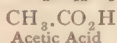


Just as in aceto-acetic acid (its esters, see above), so in malonic acid, the hydrogen atoms of the group  $\text{CH}_2$  may be replaced by alkyls, the resulting alkyllic malonic acids, when heated, also sustain a loss of carbon dioxide, with formation of alkyllic acetic acids. (*Ber.*, 13, 595.)

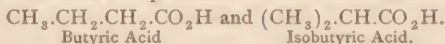
The isomerisms of the monobasic acids are influenced by the isomerisms of the hydrocarbon radicals, to which the carboxyl



group is attached. There are no possible isomerides of the first three members of the series  $C_nH_{2n}O_2$  :—

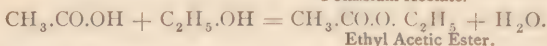


Two structural cases are possible for the fourth member,  $C_4H_8O_2$  :



Four isomerides are possible with the fifth member,  $C_5H_{10}O_2 = C_4H_9\cdot\text{CO}_2\text{H}$ , inasmuch as there are four butyl,  $C_4H_9$ , groups, etc.

The hydrogen of carboxyl replaced by metals yields salts, and when replaced by alkyls, compound ethers or esters are formed (see p. 114) :—



The residues combined in the acids with hydrogen are termed *acid radicals* :—



These are capable of entering various combinations. Their halogen derivatives, or the *haloid anhydrides* of the acids, like



are produced when the halogen derivatives of phosphorus act upon the acids or their salts (p. 65) :—

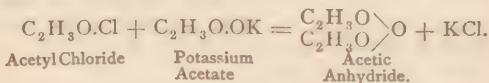


The aldehydes are the hydrides of these acid radicals, and the ketones their compounds with alcohol radicals :—



The conversion of the acids into aldehydes and ketones has already received attention. (pp. 148 and 160).

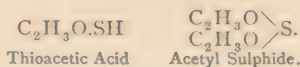
When an atom of oxygen unites two acid radicals we obtain oxides of the latter or the *acid anhydrides* :—



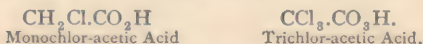
The *amides* of the acids appear by the union of the acid radicals with the amido group :—



*Sulphur Compounds*, corresponding to the acids and their anhydrides, exist :—

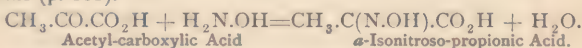


Furthermore, *substituted* acids are obtained by the direct substitution of halogens for the hydrogen of the alkyls present in the acids :—

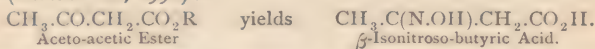


The nitro-derivatives of the fatty acids are prepared by treating some of the iod-acids with silver nitrite (see Nitropropionic acid), or by the action of nitric acid upon the fatty acids containing a tertiary CH-group (*Ber.* 15, 2318).

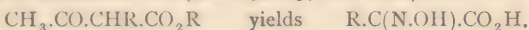
*Isonitroso-derivatives* are obtained from the ketone acids by the action of hydroxylamine (p. 161):—



In the same manner the  $\beta$ -isonitroso-acids are produced from the aceto-acetic esters (and their alkyl derivatives) by means of  $\text{H}_2\text{N}.\text{OH}$  and saponification with alkalis (*Berichte* 16, 2996) :—



Alcoholic sodium and  $\text{NaNO}_2$  acting on the monoalkylic aceto-acetic esters produce the  $\alpha$ -isonitroso-acids (*Ber.* 15, 1057, 16, 2180) :—



By reduction with tin and hydrochloric acid these derivatives become amido-acids. They do not give the nitroso-reaction with phenol and sulphuric acid (p. 79).

Of the decomposition reactions of the acids those may be mentioned again which lead to the formation of hydrocarbons.

1. The distillation of the alkali salts with alkalis or lime (see p. 46) :—



2. The electrolysis of the alkali salts in concentrated aqueous solution; hydrogen separates upon the negative pole, and carbon dioxide and the hydrocarbon upon the positive (see p. 46) :—



# 1. FATTY ACIDS, $\text{C}_n\text{H}_{2n}\text{O}_2$ .

Formic Acid	$\text{CH}_2\text{O}_2 = \text{HCO}_2\text{H}$
Acetic “	$\text{C}_2\text{H}_4\text{O}_2 = \text{CH}_3.\text{CO}_2\text{H}$
Propionic “	$\text{C}_3\text{H}_6\text{O}_2 = \text{C}_2\text{H}_5.\text{CO}_2\text{H}$
Butyric “	$\text{C}_4\text{H}_8\text{O}_2 = \text{C}_3\text{H}_7.\text{CO}_2\text{H}$
Valeric “	$\text{C}_5\text{H}_{10}\text{O}_2 = \text{C}_4\text{H}_9.\text{CO}_2\text{H}$
Caproic “	$\text{C}_6\text{H}_{12}\text{O}_2 = \text{C}_5\text{H}_{11}.\text{CO}_2\text{H}$
Enanthylic “	$\text{C}_7\text{H}_{14}\text{O}_2 = \text{C}_6\text{H}_{13}.\text{CO}_2\text{H}$

Caprylic Acid	$C_8H_{16}O_2$	+ 16°*	Pelargonic Acid	$C_9H_{18}O_2$	+ 12°
Capric "	$C_{10}H_{20}O_2$	31.4°	Undecylic "	$C_{11}H_{22}O_2$	28°
Lauric "	$C_{12}H_{24}O_2$	43.6°	Tridecylic "	$C_{13}H_{26}O_2$	40.5°
Myristic "	$C_{14}H_{28}O_2$	54°	Pentadecatoic "	$C_{15}H_{30}O_2$	51°
Palmitic "	$C_{16}H_{32}O_2$	62°	Margaric "	$C_{17}H_{34}O_2$	60°
Stearic "	$C_{18}H_{36}O_2$	69°	—	$C_{19}H_{38}O_2$	—
Arachidic "	$C_{20}H_{40}O_2$	75°	Medullic "	$C_{21}H_{42}O_2$	72°
Behenic "	$C_{22}H_{44}O_2$	73°	—	$C_{23}H_{46}O_2$	—
Lignoceric "	$C_{24}H_{48}O_2$	80.5°	Hyænic "	$C_{25}H_{50}O_2$	77°
	Cerotic Acid			$C_{27}H_{54}O_2$	79°
	Mellissic "			$C_{80}H_{60}O_2$	91°
	Theobromic "	(?)		$C_{64}H_{128}O_2$	72°

The acids of this series are known as the *fatty acids*, because their higher members occur in the natural fats and the free acids (excepting the first members) resemble fats. The latter are ester-like compounds of the fatty acids, and are chiefly esters of the trihydric glycerol. On boiling them with caustic potash or soda (saponification) alkali salts of the fatty acids are formed, and from these the mineral acids release the fatty acids.

The lower acids (with exception of the first members) are oily liquids; the higher, commencing with capric acid, are solids at ordinary temperatures. The first can be distilled without decomposition; the latter are partially decomposed, and can only be distilled without alteration in vacuo. All of them are readily volatilized with steam. Acids of like structure show an increase in their boiling temperatures of about 19° for every +  $CH_2$ . It may be remarked, in reference to the melting points, that these are higher in acids of normal structure, containing an even number of carbon atoms, than in the case of those having an odd number of carbon atoms (see above). The dibasic acids exhibit the same characteristic. As the oxygen content diminishes, the specific gravities of the acids grow successively less, and the acids themselves at the same time approach the hydrocarbons. The lower members are readily soluble in water. The solubility in the latter regularly diminishes with increasing molecular weight. All are easily soluble in alcohol, and especially so in ether. Their solutions redden blue litmus. Their acidity diminishes with increasing molecular weight; this is very forcibly expressed by the diminution of the heat of neutralization, and the initial velocity in the etherification of the acids.

A mixture of the volatile acids can be separated by fractionation only with great difficulty. It is advisable to combine this with a *partial saturation*. For instance, a mixture of two acids, *e.g.*, butyric and valeric acids, is about half saturated with potash, and the aqueous solution distilled as long as the distillate continues to react acid. If enough alkali had been added to saturate the less volatile acid (in this case valeric), the more volatile compound (butyric acid) will be almost the sole constituent of the distillate. Should the contrary be the real condition, the

\* Melting points.

distillate is subjected again to the same operation. The residue after distillation is a mixture of salts of both acids. This is true when the quantity of alkali was more than sufficient for the saturation of the less volatile acid (valeric). The acids are liberated from their salts by distillation with sulphuric acid, and the distillate again submitted to the process described above.

To be assured of the purity of the acids, the aqueous solution of their alkali salts is fractionally precipitated with silver nitrate. The less soluble silver salts (of the higher acids), are the first to separate out.

### (1) Formic Acid, $\text{CH}_2\text{O}_2 = \text{HCO.OH}$ .

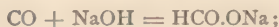
Formic acid (*Acidum formicum*) is found free in ants, in stinging nettles, in shoots of the pine, in various animal secretions, and may be obtained from these substances by distilling them with water. It is produced artificially according to the usual methods (p. 168): by the oxidation of methyl alcohol; by heating hydrocyanic acid with alkalis or acids:—



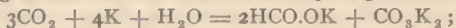
and on boiling chloroform with alcoholic potash:—



Worthy of mention, is the direct production of formates by the action of CO upon concentrated potash at  $100^\circ$ . The reaction occurs more easily if soda-lime at  $200\text{--}220^\circ$  (Ber. 13, 718) be employed:—

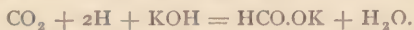


also by letting moist carbon dioxide act upon potassium:—



potassium carbonate is produced at the same time.

Formates are also formed in the action of sodium amalgam upon a concentrated aqueous ammonium carbonate solution, or with the same reagent upon aqueous primary carbonates:— $\text{CO}_3\text{KH} + \text{H}_2 = \text{HCO}_2\text{K} + \text{H}_2\text{O}$ ; likewise on boiling zinc carbonate with caustic potash and zinc dust. In all these methods it is the nascent hydrogen, which, in presence of the alkali, unites itself to carbon dioxide:—



The most practical method of preparing formic acid consists in heating oxalic acid:—

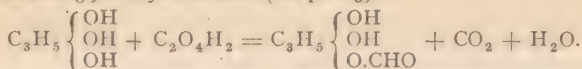


This decomposition is accelerated by the presence of glycerol, because free oxalic acid sublimes with partial decomposition.

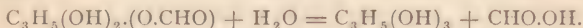
Crystallized oxalic acid ( $\text{C}_2\text{O}_4\text{H}_2 + 2\text{H}_2\text{O}$ ) is added to moist concentrated glycerol and the whole heated to  $100\text{--}110^\circ$ . Carbon dioxide is evolved and formic acid distils over. As soon as  $\text{CO}_2$  ceases generating, add more oxalic acid and heat anew, when a concentrated formic acid passes over. Continued addition of oxalic acid and the application of heat furnish a regular 56 per cent. aqueous formic acid. The mechanism of the reaction is this: on heating crys-



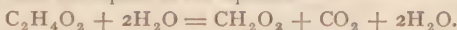
tallized oxalic acid it parts with its water of crystallization and unites with the glycerol to form *glycerol formic ester* (see p. 103):—



On further addition of oxalic acid the latter again breaks up into anhydrous acid and water, which converts the glycerol formic ester into glycerol and formic acid:—



The anhydrous oxalic acid unites anew with the regenerated glycerol to produce the formic ester. The quantities of acid and water distilling over in the latter part of the operation correspond to the equation:—



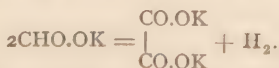
To obtain anhydrous acid, the aqueous product is boiled with PbO and the beautifully crystallized lead salt decomposed, at  $100^\circ$ , in a current of hydrogen sulphide. If anhydrous acid be employed in the reaction a 95–98 per cent. formic acid can be immediately obtained. Boron trioxide will completely dehydrate this (*Berichte*, 14, 1709).

Anhydrous formic acid is a mobile liquid, with a specific gravity of 1.223 at  $0^\circ$  and boils at  $99^\circ$ . It becomes crystalline at  $0^\circ$ , and fuses at  $+8.6^\circ$ . It has a pungent odor (from ants) and causes blisters on the skin. It mixes in all proportions with water, alcohol and ether, and yields the hydrate  $2\text{CH}_2\text{O}_2 + \text{H}_2\text{O}$ , which boils at  $105^\circ$  and dissociates into formic acid and water. Concentrated, hot sulphuric acid decomposes formic acid into carbon monoxide and water:— $\text{CH}_2\text{O}_2 = \text{CO} + \text{H}_2\text{O}$ . A temperature of  $160^\circ$  suffices to break up the acid into carbon dioxide and hydrogen. The same change may occur at ordinary temperatures by the action of pulverulent rhodium, iridium and ruthenium, but less readily when platinum sponge is employed.

According to its structure,  $\text{HCO.OH}$ , formic acid is also an aldehyde, as it contains the group  $\text{CHO}$ ; this would account for its reducing property, its ability to precipitate silver from a hot neutral solution of silver nitrate, and mercury from mercuric nitrate, the acid itself oxidizing to carbon dioxide.

The formates, excepting the difficultly soluble lead and silver salts, are readily soluble in water.

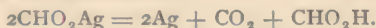
The alkali salts deliquesce in the air; heated carefully to  $250^\circ$  they become oxalates:—



By strong ignition of the resulting oxalate with an excess of alkali it decomposes with the formation of a carbonate and the liberation of hydrogen. These reactions serve for the preparation of pure hydrogen. The ammonium salt,  $\text{CHO.O.NH}_4$ , decomposes into hydrogen cyanide and water when heated to  $180^\circ$ :—



The lead salt,  $(\text{CH}_3\text{O}_2)_2\text{Pb}$ , crystallizes in brilliant needles, soluble in 36 parts of cold water. The silver salt,  $\text{CH}_3\text{O}_2\text{Ag}$ , is obtained by the double decomposition of the alkali salt with silver nitrate. It is precipitated in the form of white needles that rapidly blacken on exposure to light. When heated, it decomposes into silver, carbon dioxide and formic acid :—



The mercury salt sustains a similar decomposition.

**Monochloroformic acid**,  $\text{CClO.OH}$ , is regarded as chlor-carbonic acid.

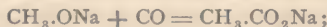
## (2) Acetic Acid, $\text{C}_2\text{H}_4\text{O}_2 = \text{CH}_3.\text{CO}_2\text{H}$ .

This acid (*Acidum aceticum*) is produced in the decay of many organic substances and in the dry distillation of wood, sugar, tartaric acid, and other compounds. It may be synthetically prepared :

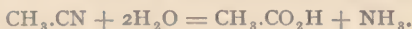
1. By the action of carbon dioxide upon sodium methyl :—



2. By heating sodium methylate with carbon monoxide to  $100^\circ$  :—



3. By boiling methyl cyanide (acetonitrile) with alkalies or acids (p. 168) :—



It is made on a large scale by the oxidation of ethyl alcohol, and by the distillation of wood.

(1) In presence of platinum sponge, the oxygen of the air converts ethyl alcohol into acetic acid; this occurs, too, in the *acetic fermentation* induced by a minute organism (*Mycoderma aceti*). The process is applied technically in the manufacture of vinegar (p. 176). Dilute aqueous solutions of whiskey, wine or starch mash are mixed with some vinegar and yeast and exposed to the air at a temperature of  $20$ – $40^\circ$ . To hasten the oxidation, proceed as follows: Large, wooden tubs are filled with shavings previously moistened with vinegar, then the diluted (10 per cent.) alcoholic solutions are poured upon these. The lower part of the tub is provided with a sieve-like bottom, and all about it are holes permitting the entrance of air to the interior. The liquid collecting on the bottom is run through the same process two or three times, to insure the conversion of all the alcohol into acetic acid. It is very evident that this process is based on accelerated oxidation, due to the increased exposure of the liquid surface to the air.

Pasteur contends that the presence of porous substances (wood shavings) is not required in the vinegar manufacture, all that is necessary being the exposure of the alcoholic fluid, mixed with *Mycoderma aceti*, to the air. (French or Orleans Method.)

(2) Considerable quantities of acetic acid are also obtained by the dry distillation of wood in cast-iron retorts. The aqueous distillate, consisting of acetic acid, wood spirit, acetone, and empyreumatic oils, is neutralized with soda, evaporated to dryness, and the residual sodium salt heated  $230^\circ$ – $250^\circ$ . In this manner, the greater portion of the various organic admixtures is destroyed, sodium acetate remaining unaltered. The salt purified in this way is distilled with sulphuric acid when acetic acid is set free and purified by further distillation over potassium chromate.

Anhydrous acetic acid at low temperatures consists of a leafy, crystalline mass, fusing at  $16.7^{\circ}$ , and forming at the same time a penetrating, acid-smelling liquid, of specific gravity 1.0514 at  $20^{\circ}$ . It boils at  $118^{\circ}$ , and mixes with water in all proportions. In this case, a contraction first ensues, consequently the specific gravity increases until the composition of the solution corresponds to the hydrate,  $C_2H_4O_2 + H_2O (= CH_3.C(OH)_3)$ ; the specific gravity then equals 1.0754 at  $15^{\circ}$ . On further dilution, the specific gravity becomes less, until a 50 per cent. solution possesses about the same specific gravity as anhydrous acetic acid. Ordinary vinegar contains about 5–15 per cent. acetic acid.

Pure acetic acid should not decolorize a drop of potassium permanganate.

*Acetates.* The acid combines with one equivalent of the bases, forming readily soluble, crystalline salts. It also yields basic salts with lead and copper; these are difficultly soluble in water. The alkali salts have the additional property of combining with a molecule of acetic acid, yielding *acid* salts,  $C_2H_3KO_2 + C_2H_4O_2$ . In this respect, acetic acid behaves like a dibasic acid. The fact that it furnishes only neutral esters proves it, however, to be only monobasic. The existence of acid salts also points to a condensation of two molecules of the acid, analogous to that occurring with the aldehydes.

*Potassium Acetate*,  $C_2H_3KO_2$ , deliquesces in the air, and dissolves readily in alcohol. Carbon dioxide will set free acetic acid and precipitate potassium carbonate in such an alcoholic solution; but in an aqueous solution, acetic acid will displace carbon dioxide from the carbonates. On adding acetic acid to neutral potassium acetate, an *acid* salt,  $C_2H_3KO_2.C_2H_4O_2$ , crystallizes out on evaporation; this consists of pearly leaflets. It fuses at  $148^{\circ}$ , and at  $200^{\circ}$  decomposes into the neutral salt and acetic acid.

*Sodium Acetate*,  $C_2H_3NaO_2 + 3H_2O$ , crystallizes in large, rhombic prisms, soluble in 2.8 parts water at medium temperatures. The crystals effloresce on exposure, and lose all their water. When heated, the anhydrous salt remains unchanged at  $310^{\circ}$ .

*Ammonium Acetate*,  $C_2H_3(NH_4)O_2$ , is obtained as a crystalline mass on saturating acetic acid with ammonia. When the aqueous solution is evaporated, the salt decomposes into acetic acid and ammonia. Heat applied to the dry salt converts it into water and acetamide,  $C_2H_3.O.NH_2$ .

*Ferrous Acetate*,  $(C_2H_3O_2)_2Fe$ , is produced on dissolving iron in acetic acid; it consists of green colored, readily soluble prisms. The aqueous solution oxidizes in the air to basic ferric acetate. Neutral ferric acetate,  $(C_2H_3O_2)_3Fe$ , is not crystallizable, and dissolves in water with a deep, reddish-brown color. On boiling, ferric oxide is precipitated in the form of basic acetate. The same may be said in regard to aluminium acetate.

*Neutral Lead Acetate*,  $(C_2H_3O_2)_2Pb + 3H_2O$ , is obtained by dissolving litharge in acetic acid. The salt affords brilliant four-sided prisms, which effloresce on exposure. It possesses a sweet taste (hence, called *sugar of lead*), and is poisonous. When heated, it melts in its water of crystallization, loses all of the latter at  $100^{\circ}$ , and at higher temperatures passes into acetone,  $CO_2$ , and lead oxide. If an aqueous solution of sugar of lead be boiled with litharge, *basic*

*lead salts* of varying lead content are produced. Their alkaline solutions find application under the designation—*lead vinegar*. Solutions of basic lead acetates absorb carbon dioxide from the air and deposit *basic carbonates* of lead—white lead.

*Neutral Copper Acetate*,  $(C_2H_3O_2)_2Cu + H_2O$ , is obtained by the solution of cupric oxide in acetic acid, and crystallizes in dark-green rhombic prisms. It is easily soluble in water. *Basic copper salts* occur in trade under the title of *verdigris*. They are obtained by dissolving copper strips in acetic acid in presence of air. The double salt of acetate and arsenite of copper is the so-called *Schweinfurt Green—mitis green*.

*Silver Acetate*,  $C_2H_3O_2Ag$ , separates in brilliant needles or leaflets when concentrated acetate solutions and silver nitrate are mixed. The salt is soluble in 98 parts water at  $14^\circ C$ .

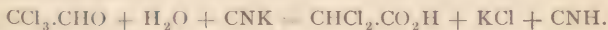
### SUBSTITUTION PRODUCTS OF ACETIC ACID.

The three hydrogen atoms of the methyl group in acetic acid can be replaced by halogens. The chlorine derivatives result by the action of chlorine in the sunlight upon acetic acid, or if chlorine be conducted into a boiling aqueous solution of the acid containing iodine (compare p. 64). It is more practicable to chlorinate acetyl chloride,  $C_2H_3O.Cl$ , and convert the product into the acids by means of water. In this way a mixture of the mono-, di- and tri-substituted acids is always formed, which are separated by fractional distillation. These are more powerful acids than acetic.

**Monochloroacetic Acid**,  $CH_2Cl.CO_2H$ , crystallizes in rhombic prisms or plates, fusing at  $62^\circ$  and boiling at  $185^\circ-187^\circ$ . The silver salt,  $C_2H_2ClO_2Ag$ , crystallizes in pearly, glistening scales, and at  $70^\circ$  decomposes into  $AgCl$  and glycolide. The *ethyl ester*,  $C_2H_2ClO_2.C_2H_5$ , obtained by conducting  $HCl$  into a mixture of the acid and absolute alcohol, boils at  $143.5^\circ$ .

When monochloroacetic acid is heated with alkalis or silver oxide, the chlorine is replaced by the hydroxyl group and we get glycollic acid ( $C_2H_3(OH)O_2$ ). Amido-acetic acid,  $CH_2(NH_2).CO_2H$ , or glycocoll, results when the monochloro acid is digested with ammonia.

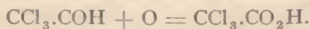
**Dichloroacetic Acid**,  $CHCl_2.CO_2H$ , is produced when chloral is heated with CNK and some water:—



It boils from  $190^\circ-191^\circ$  and solidifies below  $0^\circ$ . The free acid is best obtained by heating its potassium salt (prepared from the ethyl ester) in a current of  $HCl$  gas.

The *ethyl ester*,  $C_2HCl_2O.O.C_2H_5$ , is prepared by the action of potassium cyanide and alcohol upon chloral. (For the mechanism of this peculiar reaction, see *Ber.*, 10, 2120). It is a heavy liquid, boiling from  $156^\circ-157^\circ$ . Alcoholic potash decomposes it immediately into potassium dichloroacetate and alcohol. When the acid is boiled with aqueous potash, it breaks up into oxalic and acetic acids. The salts of the di-chloro acid reduce silver solutions, forming at first glyoxylic acid.

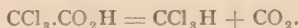
**Trichloroacetic Acid**,  $CCl_3.CO_2H$ , is made by letting chlorine act in the sunlight upon tetrachlorethylene,  $C_2Cl_4$ . It is best obtained by the oxidation of chloral with fuming nitric acid, chromic acid or potassium permanganate:—



It consists of rhombic crystals, which deliquesce, melt at  $52^\circ$ , and boil at  $195^\circ$ . It yields easily soluble, crystalline salts with bases, but on evaporation they are soon broken up. The *ethyl-ester*,  $C_2Cl_3O.O.C_2H_5$ , boils at  $164^\circ$ .



When the acid is heated with ammonia or alkalis it yields  $\text{CHCl}_3$  and carbon dioxide:—



Sodium alcoholate changes it into potassium carbonate and formate, and potassium chloride.

Nascent hydrogen (sodium amalgam) reconverts the substituted acetic acids into the original acetic acid.

The bromine substitution acids result when acetic acid is heated in sealed tubes along with bromine; the presence of  $\text{HBr}$  accelerates their formation (*Ber.*, 13, 531 and 1688). An easier procedure is to introduce bromine into acetyl-bromide and decompose the product with water.

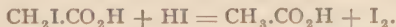
**Monobromacetic Acid**,  $\text{C}_2\text{H}_3\text{BrO}_2$  (Preparation, see *Ber.*, 16, 2502), crystallizes in deliquescent rhombohedra, and boils at  $208^\circ$ . Its *ethyl-ester*,  $\text{C}_2\text{H}_2\text{BrO}_2.\text{C}_2\text{H}_5$ , is a liquid which boils at  $159^\circ$  and suffers a slight decomposition at the same time.

**Dibromacetic Acid**,  $\text{C}_2\text{H}_2\text{Br}_2\text{O}_2$ , is a crystalline mass, melting at  $45\text{--}50^\circ$ , and boiling from  $232\text{--}235^\circ$ . Its salts are very unstable. The *Ethyl-ester*,  $\text{C}_2\text{HBr}_2\text{O}_2.\text{C}_2\text{H}_5$ , like that of the dichloracid, may be prepared from bromal with  $\text{CNK}$  and alcohol. It boils at  $192\text{--}194^\circ$ .

**Tribromacetic Acid**,  $\text{C}_2\text{HBr}_3\text{O}_2$ , made from tribromacetyl bromide,  $\text{CBr}_3.\text{COBr}$ , and by the oxidation of bromal with nitric acid, consists of table-like crystals, permanent in the air. It melts at  $133^\circ$ , and boils at about  $245^\circ$ .

The iodine substitution acids (their esters) are obtained from the chlor- and brom-acid esters when the latter are heated with potassium iodide (p. 68). They are also produced on boiling acetic acid anhydride with iodine and iodic acid (p. 64).

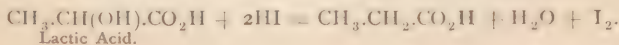
**Moniodacetic Acid**,  $\text{C}_2\text{H}_3\text{IO}_2$ , crystallizes in colorless plates, which melt at  $82^\circ$ , and decompose when more strongly heated. Its salts are unstable. The *ethyl-ester* boils at  $178\text{--}180^\circ$ . When heated with  $\text{HI}$  it passes into acetic acid (p. 64):—



**Ethyl Nitroacetic Ester**,  $\text{CH}_2(\text{NO}_2).\text{CO}_2.\text{C}_2\text{H}_5$ , is produced in the action of silver nitrite upon bromacetic ester, and boils at  $151\text{--}152^\circ$ . By reduction with tin and hydrochloric acid it yields amido-acetic acid. The free nitro-acetic acid at once decomposes into nitromethane,  $\text{CH}_3(\text{NO}_2)$ , and  $\text{CO}_2$ .

**Ethyl Isonitroso-acetic Ester**,  $\text{CH}(\text{N.OH}).\text{CO}_2.\text{C}_2\text{H}_5$  (p. 171), is produced by the action of nitric acid upon the aceto-acetic ester. It is a yellow oil, which suffers decomposition when distilled (*Annalen*, 222, 48).

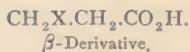
**3. Propionic Acid**,  $\text{C}_3\text{H}_6\text{O}_2 = \text{CH}_3.\text{CH}_2.\text{CO}_2\text{H}$ , may be prepared by the methods in general use in making fatty acids, and by the oxidation of normal propyl alcohol with chromic acid, or from ethyl cyanide,  $\text{C}_3\text{H}_5.\text{CN}$  (propio-nitrile) by the action of sulphuric acid (p. 168). Especially noteworthy is its formation from acrylic acid,  $\text{C}_3\text{H}_4\text{O}_2$ , through the agency of nascent hydrogen (sodium amalgam); likewise its production from lactic and glyceric acids when these are heated with hydriodic acid:—



Propionic acid is a colorless liquid, of penetrating odor, with specific gravity 0.992 at 18°, and boiling at 140°. Calcium chloride separates it from its aqueous solution, in the form of an oily liquid.

The *barium salt*,  $(C_3H_5O_2)_2, Ba + H_2O$ , crystallizes in rhombic prisms. The *silver salt*,  $C_3H_5O_2Ag$ , consists of fine needles, soluble in 119 parts water at 17°. Its *ethyl ester* boils at 98°.

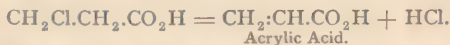
**Substitution Products.**—By the replacement of one hydrogen atom in propionic acid, two series of mono-derivatives, termed the  $\alpha$ - and  $\beta$ -derivatives, arise :—



The isomeric compounds of the higher fatty acids are similarly designated as  $\alpha$ -,  $\beta$ -,  $\gamma$ -, etc. Whenever bromine is introduced into the fatty acids, it occupies preferably the  $\alpha$ -position. In the formation of the halogen derivatives from the unsaturated acids by addition of the halogen hydride, the halogen enters in preference the  $\beta$ - or  $\gamma$ -position :—

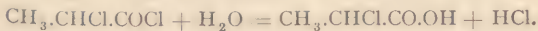


The  $\alpha$  halogen acids yield  $\alpha$ -oxy-acids when heated with aqueous bases, whereas the  $\beta$  derivatives readily part with a halogen hydride, and become unsaturated acids (*Ann.*, 219, 322) :—



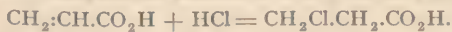
From the  $\gamma$ -acids originate salts of  $\gamma$ -oxy-acids through the action of bases. When in free condition they change to lactones. The alkaline carbonates convert them into the latter immediately.

$\alpha$ -Chlorpropionic Acid,  $C_3H_5ClO_2$ , is obtained by the decomposing action of water upon lactyl chloride (see lactic acid) :—



It is a thick liquid, of specific gravity 1.28, and boils at 186°. When heated with moist oxide of silver, it becomes lactic acid. The *ethyl ester* boils at 146°. It is obtained by the action of alcohol upon lactyl chloride.

$\beta$  Chlorpropionic Acid,  $C_3H_5ClO_2$ , is produced by the action of chlorine water upon  $\beta$ -iodpropionic acid, and the addition of HCl to acrylic acid :—



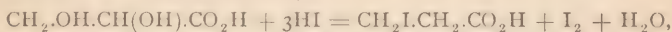
It is crystalline, and melts about 40°. The *ethyl ester* boils about 155°.

$\alpha$ -Brompropionic Acid,  $C_3H_5BrO_2$ , is produced by the direct bromination of propionic acid (*Annalen*, 216, 131), and when  $\alpha$ -lactic acid is treated with HBr. It solidifies at 17°, and boils near 202°. The *ethyl ester* boils about 162°.

$\beta$  Propionic Acid,  $C_3H_5BrO_2$ , is formed when bromine water acts on  $\beta$ -iodpropionic acid, or by the addition of HBr to acrylic acid. The acid crystallizes, and melts at 61.5°.

**$\alpha$ -Iodopropionic Acid**,  $C_3H_5IO_2$ , is produced by acting on lactic acid, with phosphorus iodide. It is an oily liquid.

**$\beta$ -Iodopropionic Acid**,  $C_3H_5IO_2$ , forms when  $PI_3$  and water are allowed to act on glyceric acid (*Ann.*, 191, 284):—



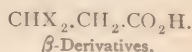
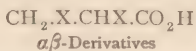
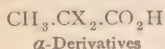
and when  $HCl$  is added to acrylic acid. The acid crystallizes in large, colorless, six-sided plates, with peculiar odor. They melt at  $82^\circ$ . Hot water dissolves the acid readily. Heated with concentrated hydriodic acid, it is reduced to propionic acid. The ethyl ester boils at  $202^\circ$  (*Ann.*, 216, 128).

**$\beta$ -Nitropropionic Acid**,  $CH_2(NO_2).CH_2.CO_2H$ . This is formed, like the nitro-paraffins (p. 79), by the action of silver nitrite upon  $\beta$ -iodopropionic acid. It is very readily soluble in water, alcohol and ether. It crystallizes from chloroform in brilliant scales, melting at  $66-67^\circ$ . Reduced with tin and hydrochloric acid it becomes  $\beta$ -amidopropionic acid. The *ethyl ester*, obtained from  $\beta$ -iodopropionic ester, boils from  $161-165^\circ$ .

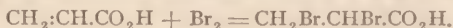
**$\alpha$ -Isonitroso-propionic Acid**,  $CH_3.C(N.OH).CO_2H$ , is a white, crystalline powder, made from acetyl carboxylic acid and methyl aceto-acetic ester (p. 171). It decomposes at  $177^\circ$  without fusing. Reduction converts it into  $\alpha$ -amidopropionic acid (Alanine).

The *ethyl ester* consists of shining crystals, melting at  $94^\circ$ , and boiling at  $233^\circ$ .

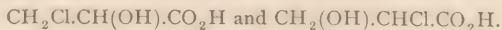
The *disubstitution products* of propionic acid may exist in three isomeric forms:—



The derivatives of the homologous acids are similarly named. The  $\alpha$ -derivatives are almost the exclusive product in the chlorination and bromination of the fatty acids or their derivatives. The addition of chlorine or bromine (best in  $CS_2$  solution) to the unsaturated acids converts them into  $\alpha\beta$  derivatives:—



Boiling water scarcely affects the  $\alpha$ -derivatives; but the  $\alpha\beta$ -compounds become halogen hydroxy-acids:—



The alkalis convert these into anhydride or ether-acids (glycide acids).

**$\alpha$ -Dichloropropionic Acid**,  $CH_3.CCl_2.CO_2H$ , is obtained from dichloropropionitrile,  $CH_3.CCl_2.CN$  (by chlorination of propionitrile), with sulphuric acid (see p. 168). The ethyl ester may be formed from pyroracemic acid,  $CH_3.CO.CO_2H$ , by the action of  $PCl_5$  and the decomposition of the chloride produced at first with alcohol. It is a liquid that boils at  $185^\circ-190^\circ$ , solidifies below  $0^\circ$ , and is volatilized in a current of steam. The ethyl ester,  $C_3H_3Cl_2.O_2.C_2H_5$ , boils at  $156^\circ-157^\circ$ ; its chloride boils at  $105^\circ-115^\circ$ , and the *amide*,  $CH_3.CCl_2.CO.NH_2$ , melts at  $116^\circ$ .

When the aqueous solutions of the  $\alpha$ -dichloropropionates are boiled, metallic chlorides and salts of  $\alpha$ -chloracrylic acid are produced. Zinc and sulphuric acid

convert the acid into propionic acid. Silver oxide changes it to  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H}$  (pyroracemic acid), while an excess of this reagent, accompanied by boiling, carries the decomposition to  $\text{CO}_2$  and acetic acid.

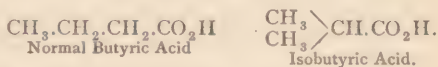
*$\alpha,\beta$ -Dichloropropionic Acid*,  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CO}_2\text{H}$ , follows from the oxidation of dichlorhydrin,  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{OH}$  (from glycerol and allyl alcohol, p. 103), also by heating  $\alpha$ -chloracrylic acid (melting at  $64^\circ$ ) to  $100^\circ$  with  $\text{HCl}$  (*Ber.*, 10, 1599). If  $\text{PCl}_5$  be allowed to act upon glyceric acid, the chloride,  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{COCl}$ , forms and this yields the ester of the  $\alpha,\beta$ -acid when treated with alcohol.  *$\alpha,\beta$ -Dichloropropionic acid* crystallizes in fine needles which melt at  $50^\circ$  and boil at  $210^\circ$ , suffering slight decomposition. The *ethyl ester* boils at  $184^\circ$ .

*$\alpha$ -Dibromopropionic Acid*,  $\text{CH}_3\cdot\text{CBr}_2\cdot\text{CO}_2\text{H}$ , is obtained by heating propionic acid or  $\alpha$  brompropionic acid with bromine. It crystallizes in quadratic tables, melting at  $67^\circ$ , and boils, with slight decomposition, at  $220^\circ$ . The *ethyl ester* is a liquid with camphor-like odor, and boils at  $190^\circ$ . The salts of the acid are tolerably stable. Zinc and sulphuric acid reduce it at once to propionic acid. Alcoholic potash changes it to  $\alpha$ -bromacrylic acid,  $\text{CH}_2\cdot\text{CBr}\cdot\text{CO}_2\text{H}$ , and the latter combines with  $\text{HBr}$  and becomes  $\alpha,\beta$ -dibromopropionic acid. When the  $\alpha$ -dibrom-acid is heated to  $100^\circ$ , with fuming  $\text{HBr}$  it is transformed into an isomeric  $\alpha,\beta$ -dibrom-acid. It is very probable that  $\alpha$ -bromacrylic acid forms at first and then takes on  $\text{HBr}$ .

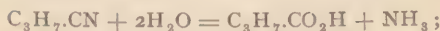
*$\alpha,\beta$ -Dibromopropionic Acid*,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ , is produced by oxidizing dibromhydrin,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{OH}$  (dibromallyl alcohol, p. 104), and acrolein dibromide (p. 159) with nitric acid; also by adding  $\text{Br}_2$  to acrylic acid and  $\text{HBr}$  to  $\alpha$ -bromacrylic acid. This compound is capable of existing in two allotropic modifications, which can be readily converted one into the other. The one form melts at  $51^\circ$ , the other, more stable, at  $64^\circ$ . The acid boils at  $227^\circ$  with partial decomposition. The *ethyl ester* has a fruit-like odor, and boils at  $211^\circ$ – $214^\circ$ . The salts are very stable. Zinc and sulphuric acid reduce the acid first to acrylic acid. Potassium iodide effects the same. Alcoholic potash changes the acid to  $\alpha$ -bromacrylic acid.

#### 4. Butyric Acids, $\text{C}_4\text{H}_8\text{O}_2$ .

Two isomeric acids are possible:—



(1) **Normal Butyric Acid**, butyric acid of fermentation, occurs free and also as the glycerol ester in the vegetable and animal kingdoms, especially in the butter of cows. It exists as hexyl ester in the oil of *Heracleum giganteum*, and as octyl ester in *Pastinaca sativa*. It is produced in the butyric fermentation of sugar, starch and lactic acid, in the decay or oxidation of normal butyl alcohol, and by the action of nascent hydrogen upon crotonic acid,  $\text{C}_4\text{H}_6\text{O}_2$ . It is prepared synthetically from propyl cyanide (butyronitrile) on boiling with alkalis or acids:—



also, from ethylic-aceto-ethyl acetate, and ethylmalonic acid (p. 169); hence the term ethyl acetic acid.



Ordinarily the acid is obtained by the fermentation of sugar or starch, induced by the previous addition of decaying substances. According to *Fitz*, the butyric fermentation of glycerol or starch is most advantageously evoked by the direct addition of schizomycetes, especially butyl-bacillus and *Bacillus subtilis* (*Ber.*, 11, 49, 53).

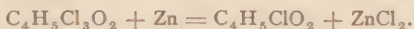
Butyric acid is a thick, rancid-smelling liquid, which solidifies when cooled. It boils at  $163^{\circ}$ ; its specific gravity equals 0.9587 at  $20^{\circ}$ . It dissolves readily in water and alcohol, and may be thrown out of solution by salts. The *ethyl ester* boils at  $120^{\circ}$ .

The butyrates dissolve readily in water. The barium salt,  $(C_4H_7O_2)_2Ba + 5H_2O$ , crystallizes in pearly leaflets. The calcium salt,  $(C_4H_7O_2)_2Ca + H_2O$  (*Ann.*, 213, 67), also yields brilliant leaflets, and is less soluble in hot than in cold water (in 3.5 parts at  $15^{\circ}$ ); therefore the latter grows turbid on warming. Silver nitrate precipitates silver butyrate in shining needles from solutions of the butyrates. It is soluble in 400 parts water at  $14^{\circ}$ .

The butyrates unite to double salts with the acetates; these behave like salts of a butyro-acetic acid,  $C_4H_8O_2.C_2H_4O_2$ . The free acid appears in the fermentation of calcium tartrate; when distilled, it breaks up into butyric and acetic acids.

A **Monochlorbutyric Acid**,  $C_4H_7ClO_2$ , is obtained in the chlorination of butyric acid in the presence of iodine. It consists of fine needles, and melts at  $99^{\circ}$ .

**Trichlorbutyric Acid**,  $C_4H_5Cl_3O_2$ , appears in the oxidation of trichlorbutyraldehyde or alcohol (p. 157), in the cold, with concentrated nitric acid, or by means of chlorine. It consists of needles, melting at  $60^{\circ}$  and soluble in 25 parts of water.  $\beta$ -Chlorcrotonic acid is formed when the trichlor-acid is boiled with zinc and water:—



Bromine converts butyric acid into  $\alpha$ -**Brombutyric Acid**,  $CH_3.CH_2.CHBr.CO.OH$ , which boils about  $215^{\circ}$ . Alcoholic potash changes this to crotonic acid. Its *ethyl ester* boils at  $178^{\circ}$ . With CNK the latter yields  $\alpha$ -cyanbutyric ester, boiling at  $208^{\circ}$ .

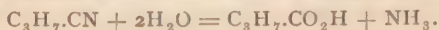
$\beta$ -**Brombutyric Acid**,  $CH_3.CHBr.CH_2.CO_2.H$ , is produced (together with a little  $\alpha$ -acid) on heating crotonic acid with hydrobromic acid. Crotonic acid combines with bromine to form  $\alpha\beta$ -dibrombutyric acid,  $CH_3.CHBr.CHBr.CO_2H$ , which melts near  $87^{\circ}$ .

$\alpha$  and  $\beta$ -**Iod-butyric Acids** are obtained by the union of crotonic acid with hydriodic acid; the first melts at  $110^{\circ}$ , the second is a liquid.

$\alpha$ -**Isonitroso-butyric Acid**,  $C_4H_5.C(N.OH).CO_2H$ , obtained from ethylic aceto-ethyl acetate (p. 171) consists of silky needles which melt with decomposition at  $152^{\circ}$ . The  $\beta$ -**Isonitroso Acid**,  $CH_3.C(N.OH).CH_2.CO_2H$ , from ethyl aceto-acetic ester and hydroxylamine, melts with decomposition at  $140^{\circ}$ .

When a saturated solution of calcium butyrate is heated for some time it slowly passes into calcium isobutyrate (*Annalen*, 181, 126).

(2) **Isobutyric Acid**,  $(CH_3)_2.CH.CO_2H$ , dimethyl-acetic acid, is found free in carobs (*Ceratonia siliqua*), as octyl ester in the oil of *Pastinaca sativa*, and as ethyl ester in croton oil. It is prepared by oxidizing isobutyl alcohol and from isopropyl cyanide:—



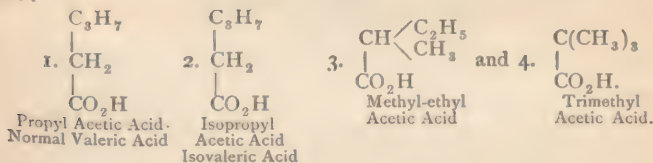
It is also obtained from dimethyl-aceto-acetic ester and from dimethyl malonic acid (p. 169), therefore the name dimethyl acetic acid.

Isobutyric acid bears great similarity to normal butyric acid, but is not miscible with water, and boils at  $155^{\circ}$ . Its specific gravity at  $20^{\circ}$  is 0.9490. It is soluble in 5 parts of water.

The *calcium salt*,  $(C_4H_7O_2)_2Ca + 5H_2O$ , crystallizes in monoclinic prisms and dissolves more readily in hot than in cold water. The silver salt,  $C_4H_7O_2Ag$ , consists of shining leaflets soluble in 110 parts  $H_2O$  at  $16^{\circ}$ . The *ethyl ester* boils at  $110^{\circ}$ ; its specific gravity = 0.89 at  $0^{\circ}$ . Potassium permanganate oxidizes it to  $\alpha$ -oxyisobutyric acid.

$\alpha$ -Bromisobutyric Acid,  $(CH_3)_2.CBr.CO_2H$ , is produced when isobutyric acid is heated with bromine to  $140^{\circ}$ . It crystallizes in white tables, melting at  $48^{\circ}$ , and boiling at  $198-200^{\circ}$ . The *ethyl ester* boils at  $163^{\circ}$  (corr.); its sp. gr. = 1.328 at  $0^{\circ}$ . Moist silver oxide or barium hydrate converts it into  $\alpha$ -oxyisobutyric acid,  $(CH_3)_2.C(OH).CO_2H$ . When boiled together with silver it affords a suberic acid,  $C_8H_{14}O_4$ —tetramethyl succinic acid.

5. Valeric Acids,  $C_5H_{10}O_2$ . There are four possible isomerides:—



(1) **Normal Valeric Acid**,  $CH_3.(CH_2)_3.CO_2H$ , formed in the oxidation of normal amyl alcohol and from butyl cyanides, is similar to butyric acid but is more difficultly soluble in water (1 part in 27 parts at  $16^{\circ}$ ). It boils at  $184-185^{\circ}$ . Its sp. gr. at  $0^{\circ}$  equals 0.957.

The  $\alpha$ -Isonitroso-acid,  $C_3H_7.C(N.OH).CO_2H$ , derived from propyl aceto-acetic ester (p. 171), melts with decomposition at  $144^{\circ}$ . The  $\gamma$  isonitroso acid,  $CH_3.C(N.OH).CH_2.CH_2.CO_2H$ , formed from lævulinic acid and hydroxylamine, fuses with decomposition at  $96^{\circ}$ .

(2) **Isovaleric Acid**,  $(CH_3)_2.CH.CH_2.CO_2H$ , isopropyl acetic acid, or isobutyl carboxylic acid, is obtained from isobutyl cyanide,  $C_4H_9.CN$ , by saponification with alkalis, likewise from isopropyl aceto-acetic ester and from isopropyl-malonic ester (see p. 169). It is an oily liquid with an odor resembling that of old cheese; possesses a specific gravity of 0.947, and boils at  $174^{\circ}$ . It is optically inactive.

The isovalerates generally have a greasy touch. When thrown in small pieces upon water they have a rotatory motion, dissolving at the same time. The *barium salt*,  $(C_5H_9O_2)_2Ba$ , usually crystallizes in thin leaflets, and is soluble in 2 parts water at  $18^{\circ}$ . The *calcium salt*,  $(C_5H_9O_2)_2Ca + 3H_2O$ , forms rather stable, readily soluble needles. The officinal *zinc salt*,  $(C_5H_9O_2)_2Zn + 2H_2O$ , crystallizes in large, brilliant leaflets; when the solution is boiled a basic salt

separates. The *silver* salt,  $C_5H_9O_2Ag$ , is very difficultly soluble in water (in 520 parts at  $21^\circ$ ). The *ethyl ester*,  $C_5H_9(C_2H_5)O_2$ , boils at  $35^\circ$ .

Potassium permanganate oxidizes isovaleric acid to  $\beta$ -oxyisovaleric acid,  $(CH_3)_2C(OH).CH_2.CO_2H$ . Nitric acid attacks in addition the  $CH$ -group, forming methyloxysuccinic acid and  $\beta$ -nitroisovaleric acid,  $(CH_3)_2C(NO_2).CH_2.CO_2H$ , which crystallizes in large leaflets and is difficultly soluble in water;  $\beta$ -dinitropropane,  $(CH_3)_2C(NO_2)_2$  (*Ber.*, 15, 2324), is produced at the same time.

Ordinary valeric acid occurs free and as esters in the animal and vegetable kingdom, chiefly in the small valerian root (*Valeriana officinalis*) and in the root of *Angelica Archangelica*, from which it may be isolated by boiling with water or a soda solution. It is a mixture of isovaleric acid with the optically active methyl-ethyl acetic acid, and is therefore also active. A similar artificial mixture may be obtained by oxidizing the amyl alcohol of fermentation (p. 99) with a chromic acid solution. Inasmuch as the salts of methyl ethyl acetic acid are very difficultly soluble, it is a general thing to obtain only isovalerates from the ordinary valeric acid. Valeric acid combines with water and yields an officinal hydrate,  $C_5H_{10}O_2 + H_2O$ , soluble in 26.5 parts of water at  $15^\circ$ .

(3) **Methyl-ethyl Acetic Acid**,  $\begin{matrix} CH_3 \\ \diagup \\ C_2H_5 \end{matrix} > CH.CO_2H$  (active valeric acid), is obtained by synthesis from methylethyl aceto-acetic ester, from methylethyl-malonic ester (p. 169) and from the so called methylethyl oxalic acid,  $\begin{matrix} CH_3 \\ \diagup \\ C_2H_5 \end{matrix} > C(OH).CO_2H$  (see this); also from methylcrotonic acid (p. 194),  $C_5H_8O_2$ , by addition of  $2H$  (when heated with  $HI$ ), and from brom- and iodmethyl-ethyl acetic acid (from methyl crotonic acid and angelic acid) by reduction with sodium amalgam.

The acid possesses a valerian-like odor, boils at  $175^\circ$  and has a specific gravity of 0.941 at  $21^\circ$ . The *calcium* salt,  $(C_5H_9O_2)_2Ca + 5H_2O$ , crystallizes in brilliant needles which slowly effloresce in the air. The *barium* salt,  $(C_5H_9O_2)_2Ba$ , is a *gummy amorphous* mass, and is not crystallizable. The *silver* salt,  $C_5H_9O_2Ag$ , is much more soluble than that of the isovaleric acid (in 88 parts at  $20^\circ$ ) and crystallizes in groups of feather-shaped, shining needles.

The synthesized methyl-ethyl acetic acid is optically inactive. An *active modification* is present in the naturally occurring valeric acid, and is obtained by the oxidation of the amyl alcohol of fermentation (see above). The silver salt affords a means of separating it from the accompanying isovaleric acid (*Annalen*, 204, 159). The active acid has not yet been isolated in a pure condition; otherwise it exhibits all the properties of the inactive variety and affords perfectly similar salts.

(4) **Trimethyl Acetic Acid**,  $(CH_3)_3C.CO_2H$  (Pinalic acid), is formed from tertiary butyl iodide,  $(CH_3)_3CI$  (p. 98), by means of the cyanide, also by the oxidation of pinacoline (p. 167). It is a leafy, crystalline mass, melting at  $35^\circ$  and boiling at  $163^\circ$ . The acid is soluble in 40 parts  $H_2O$  at  $20^\circ$  and has an odor resembling that of acetic acid.

The *barium* salt,  $(C_5H_9O_2)_2Ba + 5H_2O$ , and *calcium* salt,  $(C_5H_9O_2)_2Ca + 5H_2O$ , crystallize in needles or prisms. The *silver* salt,  $C_5H_9O_2Ag$ , is precipitated in glistening, flat needles. The *ethyl ester*,  $C_5H_9O_2.C_2H_5$ , boils at  $118.5^\circ$ .

**The Hexoic or Caproic Acids,  $C_6H_{12}O_2 = C_5H_{11}.CO_2H$ .**

Eight isomerides are theoretically possible (because there are eight  $C_5H_{11}$  (amyl) groups). Seven of these have been prepared. We may mention:—

(1) **Normal Caproic Acid or Hexoic Acid**,  $CH_3(CH_2)_4.CO_2H$ , which is produced in the fermentation of butyric acid and may also be obtained by the oxidation of normal hexyl alcohol and from normal amyl cyanide,  $C_5H_{11}.CN$ . It is an oily liquid that has a sp. gr. of 0.928 at  $20^\circ$ , boils at  $205^\circ$ , solidifies in the cold and melts at  $-2^\circ$ . Its *barium* salt,  $(C_6H_{11}O_2)_2Ba + 3H_2O$ , is soluble in 9 parts of water at  $10^\circ$ . The *ethyl ester* boils at  $167^\circ$ .

(2) **Isobutyl Acetic Acid**,  $(CH_3)_2.CH.CH_2.CO_2H$ , is obtained from isoamyl cyanide and from isobutyl aceto-acetic ester (p. 169). Some fats apparently contain it. It has a specific gravity of 0.931 at  $15^\circ$  and boils at  $200^\circ$ . The *ethyl ester* boils at  $161^\circ$ . By the oxidation of isobutyl acetic acid with potassium permanganate the lactone of  $\gamma$ -oxy-isocaproic acid,  $(CH_3)_2.C(OH).CH_2.CH_2.CO_2H$ , is formed.

(3) **Methylpropyl Acetic Acid**,  $\begin{matrix} C_3H_7 \\ CH_3 \end{matrix} > CH.CO_2H$ , is prepared from methylpropyl carbinol (p. 100) through the cyanide and from  $\alpha$ -methyl valerolactone (from saccharin) by reduction with HI. It boils at  $193^\circ$  and has the specific gravity 0.941 at  $0^\circ$  (*Ber.*, 16, 1823).

**Heptoic Acids,  $C_7H_{14}O_2 = C_6H_{13}.CO_2H$ .**

Six of the seventeen possible isomerides are known.

**Normal Heptoic or Ceananthic Acid**,  $CH_3(C_2H_5)_2.CO_2H$ , is produced by the oxidation of ceanthol (p. 158) with nitric acid, and also from normal hexyl cyanide,  $C_6H_{13}.CN$ . It is a fatty-smelling oil, boiling near  $223^\circ$ , and solidifying, when cooled, to a crystalline mass, which melts at  $-10.5^\circ$ . The *ethyl ester* boils at  $188^\circ$ .

The **Octoic Acids**,  $C_8H_{16}O_2 = C_7H_{15}.CO_2H$ .

**Normal Octoic or Caprylic Acid** is present in fusel oil, and as glycerol ester in many oils and fats. It is produced by the oxidation of fats and oleic acid with nitric acid; also obtained from normal octyl alcohol. The acid crystallizes in needles or leaflets, which melt at  $16^\circ$ – $17^\circ$ , and boil at  $236^\circ$ – $237^\circ$ . The *barium* salt is soluble in 50 parts boiling water, and crystallizes in fatty tablets.

**Nonoic Acid**,  $C_9H_{18}O_2$ , **Pelargonic Acid**, occurs in the leaves of *Pelargonium roseum*, and is prepared by the oxidation of oleic acid and oil of rue (methylnonyl ketone, p. 167), with nitric acid. It may also be obtained from normal octyl cyanide,  $C_8H_{17}.CN$ , and by the fusion of undecylenic acid (p. 195) with potassium hydroxide. It is, therefore, the normal nonoic acid. It fuses at  $+12.5^\circ$  and boils at  $253^\circ$ – $254^\circ$ .

## HIGHER FATTY ACIDS.

These (p. 172) are chiefly solids at ordinary temperatures, and can, as a general thing, be distilled without suffering decomposition. They are volatilized by superheated steam. They are insoluble in water, but readily soluble in alcohol and ether, from which they may be crystallized out. In the naturally occurring oils and solid fats, they exist in the form of glycerol esters (see these). When



fats are saponified by potassium or sodium hydroxide, salts of the fatty acids—*soaps*—are produced. The sodium salts are solids and hard, while those with potassium are soft. Salt will convert potash soaps into sodium soaps. In small quantities of water the salts of the alkalies dissolve completely, but with an excess of water they suffer decomposition, some alkali and fatty acid being liberated. The action of soap depends on this fact. The remaining metallic salts of the fatty acids are difficultly soluble or insoluble in water, but generally dissolve in alcohol. The lead salts, formed directly by boiling fats with litharge and water, constitute the so-called *lead plaster*.

The natural fats almost invariably contain several fatty acids (frequently, too, oleic acid). To separate them, the acids are set free from their alkali salts by means of hydrochloric acid and then fractionally crystallized from alcohol. The higher, less soluble acids separate out first. The separation is more complete if the acids be fractionally precipitated (see p. 173). The free acids are dissolved in alcohol, saturated with ammonium hydrate and an alcoholic solution of magnesium acetate added. The magnesium salt of the higher acid will separate out first, this is then filtered off and the solution again precipitated with magnesium acetate. The acids obtained from the several fractions are subjected anew to the same treatment, until, by further fractionation, the melting point of the acid remains constant—an indication of purity. The melting point of a mixture of two fatty acids is usually lower than the melting points of both acids (the same is the case with alloys of the metals).

The fatty acids existing in fats and oils all possess the normal structure of the carbon chains, inasmuch as they yield only lower and normal acids when oxidized. It is an interesting fact, that in the natural fats only acids exist that have an even number of carbon atoms. Those that possess an uneven number of carbon atoms (as undecylic and tridecylic) are artificially prepared by the oxidation of their corresponding ketones (p. 161). The latter are obtained by distilling the calcium salt of an acid having one carbon atom more, with calcium acetate. In this manner there is derived from lauric acid,  $C_{11}H_{23}.CO_2H$ , the ketone,  $C_{11}H_{23}.CO.CH_3$ , which is oxidized to undecylic acid,  $C_{11}H_{22}O_2 = C_{10}H_{21}.CO_2H$ , by chromic acid. Undecylic acid yields the ketone,  $C_{10}H_{21}.CO.CH_3$ , and this the acid,  $C_{10}H_{20}O_2$ , etc. Thus, starting with the highest acid, we can successively form all the lower members of the series.

**Capric Acid**,  $C_{10}H_{20}O_2$ , present in butter, in cocoanut oil and in many fats, forms a crystalline mass, melting at  $31.4^\circ$ , and boiling, with partial decomposition, at  $268^\circ$ – $270^\circ$ . The *barium* salt crystallizes from alcohol in fatty, shining needles or scales. The *ethyl ester* is a liquid, and possesses a fruit-like odor. It boils at  $243^\circ$ .

**Undecylic Acid**,  $C_{11}H_{22}O_2$ , is obtained by oxidation from undecylmethyl ketone,  $C_{11}H_{23}.CO.CH_3$  (see above), and from undecylenic acid, when the latter is heated with hydriodic acid. It is a scaly, crystalline mass, which melts at  $28.5^\circ$ , and boils at  $212^\circ$  under a pressure of 100 mm. An acid obtained from the fruit of the California bay-tree appears to be identical with the preceding acid.

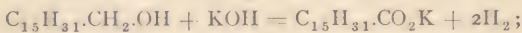
**Lauric Acid**,  $C_{12}H_{24}O_2$ , occurs as glycerol-ester in the fruit of *Laurus nobilis* and in pichurium beans. It crystallizes in large, brilliant needles which melt at  $43.6^\circ$ . The *ethyl ester* possesses a fruit-like odor, and boils at  $269^\circ$ .

**Tridecylic Acid**,  $C_{13}H_{26}O_2$ , is formed by the oxidation of tridecylmethyl ketone,  $C_{13}H_{27}CO.CH_3$  (from myristic acid), and crystallizes in scales, which melt at  $40.5^\circ$  and under 100 mm. pressure boil at  $235^\circ$ .

**Myristic Acid**,  $C_{14}H_{28}O_2$ , obtained from muscat butter (from *Myristica moschata*), from spermaceti and oil of cocoanut, is a shining, crystalline mass, which melts at  $54^\circ$ . The *ethyl ester* is solid.

**Pentadecatoic Acid**,  $C_{15}H_{30}O_2$ , is prepared from pentadecato-methyl ketone,  $C_{15}H_{31}CO.CH_3$  (from palmitic acid); it melts at  $51^\circ$ , and boils under a pressure of 100 mm. at  $257^\circ$ .

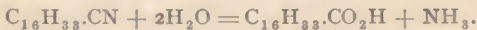
**Palmitic Acid**,  $C_{16}H_{32}O_2$  The glycerol-ester of this acid and that of stearic acid constitute the principal ingredients of solid animal fats. The stearin employed in the candle manufacture is a mixture of free palmitic and stearic acids. Palmitic acid occurs in rather large quantities, partly uncombined, in palm oil. Spermaceti is the cetyl-ester of the acid, while the myricyl ester is the chief constituent of beeswax. The acid is most advantageously obtained from olive oil, which consists almost exclusively of the glycerides of palmitic and oleic acid (see latter). The acid is artificially made by heating cetyl alcohol with soda-lime:—



also by fusing together oleic acid and potassium hydroxide.

Palmitic acid crystallizes in white needles, which melt at  $62^\circ$ , and solidify to a crystalline mass.

**Margaric Acid**,  $C_{17}H_{34}O_2$ , does not apparently exist naturally in the fats. It is made in an artificial way by boiling cetyl cyanide with caustic potash:—



The acid bears great resemblance to palmitic acid, and melts at  $59.9^\circ$ .

**Stearic Acid**,  $C_{18}H_{36}O_2$ , is associated with palmitic and oleic acids as a mixed ether in solid animal fats, the tallows. The acid crystallizes from alcohol in brilliant leaflets, which melt at  $69.2^\circ$ .

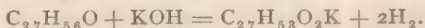
The so-called *stearin* of candles consists of a mixture of stearic and palmitic acids. For its preparation, beef tallow and suet, both solid fats, are saponified with potassium hydroxide or sulphuric acid. The acids which separate are distilled with superheated steam. The yellow, semi-solid distillate, a mixture of stearic, palmitic and oleic acids, is freed from the liquid oleic acid by pressing it between warm plates. The residual, solid mass is then fused together with some wax or paraffin, to prevent crystallization occurring when the mass is cold, and molded into candles.

**Cetyl Acetic Acid**,  $C_{16}H_{33}.CH_2.CO_2H$ , is probably identical with the above, and is obtained from cetylaceto-acetic ester and cetyl malonic acid (see p. 169). Its melting point lies near  $63^\circ$ . An isomeric acid, called *dioctyl acetic acid* ( $C_8H_{17}.CH_2.CO_2H$ ), is prepared from dioctyl-aceto-acetic ester and from dioctylmalonic acid. It melts at  $38.5^\circ$ .

We may briefly mention the following higher acids (see p. 172):—

**Arachidic Acid**,  $C_{20}H_{40}O_2$ , occurs in earth-nut oil (from *Arachis hypogaea*) and is composed of shining leaflets, melting at  $75^\circ$ .

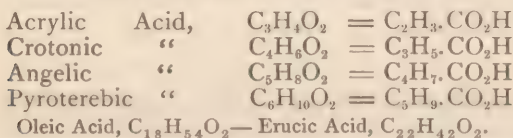
**Cerotic Acid**,  $C_{27}H_{54}O_2$ , occurs in a free condition in beeswax, and may be extracted from this on boiling with alcohol. As ceryl ester, it constitutes the chief ingredient of *Chinese wax*. On boiling the latter with an alcoholic potash solution, potassium cerotate and ceryl alcohol are produced. The acid may also be obtained by oxidizing ceryl alcohol or by fusing it with KOH:—



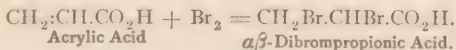
It crystallizes from alcohol in delicate needles which melt at  $78^\circ$ .

**Melissic Acid**,  $C_{30}H_{60}O_2$ , is formed from myricyl alcohol (p. 103) when the latter is heated with soda-lime. It is a waxy substance, which melts at  $88^\circ$ , but is really, as it appears, a mixture of two acids. The so-called **Theobromic Acid**,  $C_{64}H_{128}O_2$ , obtained from cacao butter, melts at  $72^\circ$  and is apparently identical with arachidic acid.

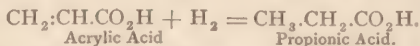
## 2. UNSATURATED ACIDS, $C_nH_{2n-2}O_2$ .



The acids of this series, bearing the name *Oleic Acids*, differ from the fatty acids by containing two atoms of hydrogen less than the latter. They also bear the same relation to them that the alcohols of the allyl series do to the normal alcohols. We can consider them derivatives of the alkylens,  $C_nH_{2n}$ , produced by the replacement of one atom of hydrogen by the carboxyl group. In this manner their possible isomerides are readily deduced. As unsaturated compounds the oleic acids are capable of combining directly with two affinities, when the double union of the two carbon atoms becomes simple. Hence they unite directly with the halogens and halogen hydrides:—



On combining with two hydrogen atoms they become fatty acids:—

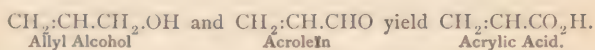


The lower members, as a general thing, combine readily with the  $H_2$  evolved in the action of zinc upon dilute sulphuric acid; while the higher remain unaffected. All may be hydrogenized, however, by heating with hydriodic acid and phosphorus. The union with halogen hydrides occurs somewhat differently

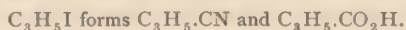
than observed with the alkylens. The halogen atom does not, as in the latter instance, attach (p. 64) itself to the carbon atom carrying the least number of hydrogen atoms, but prefers the  $\beta$  or  $\gamma$  position (p. 179).

The methods employed for the preparation of the unsaturated acids are similar to those used with the fatty acids, since the latter can be obtained from the unsaturated compounds by analogous methods. They are formed from the saturated fatty acids by the withdrawal of two hydrogen atoms, just as the alkylens are derived from the normal hydrocarbons:—

(1) Like the fatty acids they are produced by the oxidation of their corresponding alcohols and aldehydes; thus allyl alcohol and its aldehyde afford acrylic acid:—



(2) Some may be prepared synthetically from the halogen derivatives,  $\text{C}_n\text{H}_{2n-1}\text{X}$ , aided by the cyanides (see p. 168); thus allyl iodide yields allyl cyanide and crotonic acid:—

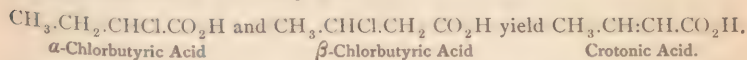


The replacement of the halogen by CN in the compounds  $\text{C}_n\text{H}_{2n-1}\text{X}$  is conditioned by the structure of the latter. Although allyl iodide,  $\text{CH}_2\text{:CH.CH}_2\text{I}$ , yields a cyanide, ethylene chloride,  $\text{CH}_2\text{:CHCl}$ , and  $\beta$ -chlorpropylene,  $\text{CH}_3\text{.CCl:CH}_2$ , are not capable of this reaction.

(3) Another synthetic method is to introduce the allyl group,  $\text{C}_3\text{H}_5$  (by means of allyl iodide), into aceto-acetic ester and malonic ester, and then further transpose the products first formed (p. 169). Allyl acetic acid,  $\text{C}_3\text{H}_5\text{.CH}_2\text{.CO}_2\text{H}$ , and diallyl acetic acid,  $(\text{C}_3\text{H}_5)_2\text{CH.CO}_2\text{H}$ , have been obtained in this manner.

Generally, the unsaturated acids are prepared from the saturated by

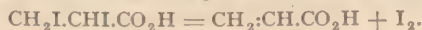
(1) The action of alcoholic potash (p. 61) upon the monohalogen derivatives of the fatty acids:—



The  $\beta$ -derivatives are especially reactive, sometimes parting with halogen hydrides on boiling with water (p. 179). (The  $\gamma$ -halogen acids yield oxy-acids and lactones.) Similarly, the  $\alpha\beta$ -derivatives of the acids (p. 180) readily lose two halogen atoms, either by the action of nascent hydrogen—



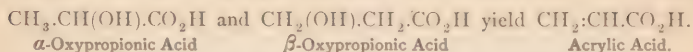
or even more readily when heated with a solution of potassium iodide, in which instance the primary di-iod compounds part with iodine (p. 71):—



(2) The removal of water (in the same manner in which the

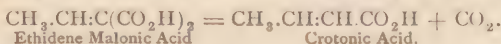


alkylens  $C_nH_{2n}$  are formed from the alcohols) from the oxy-fatty acids (the acids belonging to the lactic series):—

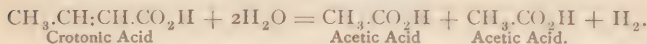
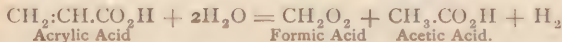


Here again the  $\beta$ -derivatives are most inclined to alteration, losing water when heated. The removal of water from the  $\alpha$ -derivatives is best accomplished by acting on the esters with  $PCl_5$ . The esters of the unsaturated acids are formed first, and can be saponified by means of alkalies.

(3) From the unsaturated dicarboxylic acids, containing two carboxyl groups attached to one carbon atom (see p. 169):—



Like the saturated acids in their entire character, the unsaturated derivatives are, however, distinguished by their power to take up additional atoms (p. 188). Their behavior, when fused with potassium or sodium hydroxide, is interesting, because it affords a means of ascertaining their structure. By this treatment their double union is severed and two monobasic fatty acids result:—



Oxidizing agents (chromic acid, nitric acid, permanganate of potash) have the same effect. The group linked to carboxyl is usually further oxidized, and thus a dibasic acid results (see p. 56).

When the unsaturated acids are heated to  $100^\circ$ , with KOH or NaOH, they frequently absorb the elements of water and pass into oxy-acids. Thus, from acrylic acid we obtain  $\alpha$ -lactic acid ( $CH_2:CH.CO_2H + H_2O = CH_3.CH(OH).CO_2H$ ), and malic from fumaric acid, etc.

**1. Acrylic Acid**,  $C_3H_4O_2 = CH_2:CH.CO_2H$ , the lowest member of this series is obtained according to the general methods:—

(1) From iod-propionic acid by the action of alcoholic potash or lead oxide.

(2) From  $\alpha,\beta$ -dibrompropionic acid by the action of zinc and sulphuric acid, or potassium iodide.

(3) By heating  $\beta$ -oxypropionic acid (hydracrylic acid).

The best method consists in oxidizing acrolein with silver oxide.

The aqueous solution (3 parts  $H_2O$ ) of acrolein is mixed with silver oxide, digested for some time in the cold and then heated to boiling. Sodium carbonate

is next added, the filtrate concentrated and distilled with dilute sulphuric acid. The acrylic acid in the distillate is converted into the silver or lead salt, which is decomposed by heating in a current of  $H_2S$ , that the acid may be obtained in an anhydrous condition.

Acrylic acid is a liquid with an odor like that of acetic acid, and solidifies at low temperatures to crystals melting at  $+7^\circ$ . It boils at  $139-140^\circ$ , and is miscible with water. If allowed to stand for some time it is transformed into a solid polymeride. By protracted heating on the water bath with zinc and sulphuric acid it is converted into propionic acid. This change does not occur in the cold. It combines with bromine to form  $\alpha\beta$ -dibromopropionic acid, and with the halogen hydrides to yield  $\beta$ -substitution products of propionic acid (p. 179). If used with caustic alkalies it is broken up into acetic and formic acids.

The salts of acrylic acid, the silver salt excepted, are very soluble in water and crystallized with difficulty. They suffer decomposition when heated to  $100^\circ$ . The *silver salt*,  $C_3H_3O_2Ag$ , consists of shining needles which blacken at  $100^\circ$ . The *lead salt*,  $(C_3H_3O_2)_2Pb$ , crystallizes in long, silky, glistening needles.

The *ethyl ester*,  $C_3H_3O_2.C_2H_5$ , obtained from the ester of  $\alpha\beta$ -dibromopropionic acid by means of zinc and sulphuric acid, is a pungent-smelling liquid which boils at  $101-102^\circ$ . The *methyl ester* boils at  $85^\circ$ , and after some time polymerizes to a solid mass.

*Substitution Products.* There are two isomeric forms of mono-substituted acrylic acids (p. 179):—



$\alpha$ -Derivatives

$\beta$ -Derivatives.

**$\alpha$ -Chloracrylic Acid** is probably the acid which results when  $\alpha\beta$ -dichloropropionic acid is heated with alcoholic potash. It crystallizes in needles, melts from  $64-65^\circ$ , and is even volatile at ordinary temperatures. It combines with  $HCl$  at  $100^\circ$  to produce  $\alpha\beta$ -dichloropropionic acid (*Ber.*, 10, 1499). The liquid chloracrylic acid (*Ibid.*, 10, 1948), formed from  $\alpha$ -dichloropropionic acid, appears to be a mixture.

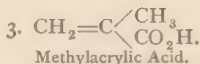
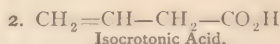
**$\beta$ -Chloracrylic Acid** is produced together with dichloracrylic acid in the reduction of chloralid with zinc and hydrochloric acid, also from propiolic acid,  $C_3H_2O_2$  (p. 197), by the addition of  $HCl$ . It crystallizes in leaflets and melts at  $84^\circ$  (*Ann.*, 203, 83). The *ethyl ester* boils at  $142-144^\circ$ , and is most easily obtained from the ester of trichlorolactic acid by reduction with zinc and hydrochloric acid in alcoholic solution. The *ester* of dichloracrylic acid is obtained at the same time.

**$\alpha$ -Bromacrylic Acid** is prepared from  $\alpha$ - and  $\alpha\beta$ -dibromopropionic acids with alcoholic potash (*Ber.*, 14, 1867). It crystallizes in large plates melting at  $69-70^\circ$ . It combines with  $HBr$  to form  $\alpha\beta$ -dibromopropionic acid.

**$\beta$ -Bromacrylic Acid** is obtained from the chloralid of tribromolactic acid when this is reduced with zinc and hydrochloric acid. It may also be prepared from propionic acid. It consists of fine needles, melting at  $115-116^\circ$ .

2. THE CROTONIC ACIDS,  $C_4H_6O_2 = C_3H_5.CO_2H$ .

According to the current representations of the constitution of the unsaturated monocarboxylic acids three isomerides of the above formula are possible:—\*



## 1. Ordinary Crotonic Acid is obtained:—

(1) By the oxidation of crotonaldehyde,  $CH_3.CH:CH.CO.H$  (p. 159).

(2) By the dry distillation of  $\beta$ -oxybutyric acid,  $CH_3.CH(OH).CH_2.CO_2H$ .

(3) By the action of alcoholic potash upon  $\alpha$ -brombutyric acid, and KI upon  $\alpha\beta$ -dibrombutyric acid.

(4) From allyl iodide by means of the cyanide.

The cyanide,  $CH_2:CH.CH_2.CN$ , obtained from allyl iodide,  $CH_2:CH.CH_2I$ , should really afford isocrotonic acid, but the reaction occurs after such a manner, that upon saponifying the cyanide with hydrochloric acid, there is a simultaneous addition of the latter, yielding first  $\beta$ -chlorbutyric acid,  $CH_3.CHCl.CH_2.CO_2H$ , which subsequently parts with HCl and becomes ordinary crotonic acid. In the same way on decomposing the cyanide with alkalis,  $\beta$ -oxybutyric acid,  $CH_3.CH(OH).CH_2.CO_2H$ , is the first product, and it then loses water (see p. 189, and *Ber.*, 12, 2056.)

The most practicable method of obtaining crotonic acid is to heat malonic acid,  $CH_2(CO_2H)_2$ , with paraldehyde and acetic anhydride. The ethidene malonic acid first produced decomposes into  $CO_2$  and crotonic acid (p. 190) (*Annalen*, 218, 147).

Crotonic acid crystallizes in fine, woolly needles or in large plates, which fuse at  $72^\circ$  and boil at  $182^\circ$ . It dissolves in 12 parts water at  $20^\circ$ . Zinc and sulphuric acid, but not sodium amalgam, convert it into normal butyric acid. It combines with HBr and HI to yield  $\beta$ -brom- and iodbutyric acid, and with bromine to  $\alpha,\beta$ -dibrombutyric acid. When fused with caustic potash, it breaks up into two molecules of acetic acid; nitric acid oxidizes it to acetic and oxalic acids.

$\alpha$ -Chlorcrotonic Acid,  $CH_3.CH:CCl.CO_2H$ , is obtained when trichlorbutyric acid (p. 182) is treated with zinc and hydrochloric acid, or zinc dust and water. It melts at  $97.5^\circ$ , boils at  $212^\circ$ , and is not affected when boiled with alkalis (see below).

\*A supposed fourth crotonic acid, the so-called vinyl acetic acid (from the so-called vinylmalonic acid) appears identical with trimethyl carboxylic acid derived from trimethylene (see p. 28).

**$\beta$ -Chlorcrotonic Acid**,  $\text{CH}_3\cdot\text{CCl}\cdot\text{CH}\cdot\text{CO}_2\text{H}(?)$ , is obtained in small quantities (together with chlorisocrotonic acid) from aceto-acetic ester. It melts at  $94.5^\circ$  and boils at  $208^\circ$ . Sodium amalgam reduces it to crotonic acid, and with boiling alkalis it yields tetrolic acid (p. 197), which unites with  $\text{HCl}$  and again forms  $\beta$ -chlorcrotonic acid.

**$\alpha$ -Bromcrotonic Acid**, from  $\alpha$ -dibrombutyric acid, melts at  $106.5^\circ$ .  **$\beta$ -Bromcrotonic Acid**, from the  $\alpha,\beta$ -dibrombutyric acid, melts at  $92^\circ$  (*Ber.*, 15, 49).

(2) **Isocrotonic Acid**,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}(?)$ , is obtained from  $\beta$ -chlorisocrotonic acid by the action of sodium amalgam. It is a liquid which does not solidify; boils at  $172^\circ$ , and has a specific gravity of 1.018 at  $25^\circ$ . When heated to  $170^\circ$ – $180^\circ$ , in a sealed tube, it changes to ordinary crotonic acid. This alteration occurs partially, even during distillation. This explains why upon fusing isocrotonic acid with  $\text{KOH}$ , formic and propionic acid (which might be expected), are not produced, but in their stead acetic acid, the decomposition product of crotonic acid. Sodium amalgam does not change it. It combines with  $\text{HBr}$ , even at ordinary temperatures, to yield brombutyric acid,  $\text{C}_4\text{H}_7\text{BrO}_2$ , which decomposes into  $\text{HBr}$  and ordinary crotonic acid when heated with water. Sodium amalgam converts this acid into butyric acid.

When  $\text{PCl}_5$  and water act upon aceto-acetic ester,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_2\text{H}_5$ , chlorisocrotonic acid (with  $\beta$ -chlorcrotonic acid) is produced. It is very probable that  $\beta$ -dichlorbutyric acid is formed at first, and this afterwards parts with  $\text{HCl}$ :—



The former melts at  $94.5^\circ$  and boils at  $208^\circ$  (see above); the latter melts at  $59.5^\circ$  and boils at  $195^\circ$ . Recent research proves that both acids possess the same constitution, because they afford like transposition products. By prolonged heating the former changes to the latter. (*Annalen*, 219, 361.)

(3) **Methacrylic Acid**,  $\text{CH}_2\text{:C}\begin{smallmatrix} \text{CH}_3 \\ \text{CO}_2\text{H} \end{smallmatrix}$ . Its ethyl ester was first obtained by the action of  $\text{PCl}_5$  upon oxy-isobutyric ester,  $(\text{CH}_3)_2\text{C}(\text{OH})\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$ . It is, however, best prepared by boiling citrabrom-pyrotartaric acid (from citraconic acid and  $\text{HBr}$ ) with water or a sodium carbonate solution:—



It consists of prisms that are readily soluble in water, fuse at  $+16^\circ$ , and boil at  $160.5^\circ$ .  $\text{NaHg}$  converts the acid into isobutyric acid. It combines with  $\text{HBr}$  and  $\text{HI}$  to form  $\alpha$ -brom- and iod-isobutyric acid, and with bromine to form  $\alpha,\beta$ -dibrom-isobutyric acid, which confirms the assumed constitution (*Journ. pr. Chemie.*, 25, 369). When fused with  $\text{KOH}$ , it breaks up into propionic and acetic acids.

### 3. ACIDS OF FORMULA $\text{C}_5\text{H}_8\text{O}_2 = \text{C}_4\text{H}_7\cdot\text{CO}_2\text{H}$ .

1. **Angelic Acid**,  $\text{C}_4\text{H}_7\cdot\text{CO}_2\text{H}$ , exists free along with valeric and acetic acids in the roots of *Angelica archangelica*, and as butyl and amyl esters in Roman oil of cumin.

To prepare the acid, boil the angelica roots with milk of lime, and distil the solution of the calcium salt with sulphuric acid. From the oily distillate, containing acetic, valeric and angelic acids, the latter crystallizes on cooling. The saponification of Roman cumin oil with potash, also furnishes the acid.



Roman oil of cumin (from *Artemis nobilis*) contains the esters of several acids. The following fractions may be obtained from that portion of it which boils up to  $210^{\circ}$ :—

1. Isobutyl butyrate, boiling  $147-148^{\circ}$ .
2. " angelate, "  $177-178^{\circ}$ .
3. Amyl angelate, "  $200-201^{\circ}$ .
4. Amyl tiglate, "  $204-205^{\circ}$ .

When these esters are saponified and distilled with sulphuric acid, the free acids are obtained. We can separate angelic and tiglic acids by means of the calcium salts, that of the first being very readily soluble in cold water.

Angelic acid crystallizes in shining prisms, melts at  $45^{\circ}$ , and boils at  $185^{\circ}$ . When boiled for some time it is converted into tiglic acid. Concentrated sulphuric acid at  $100^{\circ}$ , effects the same. The acid dissolves readily in hot water and alcohol. It is volatile with steam.

The constitution of angelic acid has not yet been explained. Isomeric relations, similar to those observed with the chlor-crotonic acids, maleic and fumaric acids, appear to exist, and for these the present structural formulas give no expression. Judging from all its transformations, angelic acid is perfectly similar to tiglic acid. Like the latter, it breaks up, when fused with KOH, into acetic and crotonic acids; when heated with HI and phosphorus, it yields methyl-ethyl acetic acid, and affords the same addition products with HBr and bromine. It is only with hydriodic acid, that it affords a different addition product, yet this has the same transformations as the HI-derivative of tiglic acid. Therefore, for the present, we must ascribe the same formula to angelic acid that is accredited to tiglic acid (*Ann.*, **216**, 161.)

2. **Methylcrotonic Acid**,  $\text{CH}_3\text{CH}:\text{C}\begin{smallmatrix} \text{CH}_3 \\ \text{CO}_2\text{H} \end{smallmatrix}$ , **Tiglic Acid**, present in Roman oil of cumin (see above), and in croton oil (from *Croton tiglium*), is a mixture of glycerol esters of various fatty and oleic acids. It is obtained artificially by acting with  $\text{PCl}_3$  upon methyl-ethyl oxy-acetic acid,  $\text{CH}_3\text{CH}_2\text{C}(\text{OH})\text{CO}_2\text{H}$  (its ester), and from  $\alpha$ -methyl- $\beta$ -oxybutyric acid,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$ , on heating the latter with hydriodic acid.

Tiglic acid crystallizes in prisms or tables, is soluble with difficulty in water, melts at  $64.5^{\circ}$ , and boils at  $198^{\circ}$ . When heated to  $160^{\circ}$  together with hydriodic acid and phosphorus, it is converted into methyl-ethyl-acetic acid (p. 184). If it be fused with KOH, it yields acetic and propionic acids. It combines with  $\text{Br}_2$ , HI and HCl to form substitution products of methyl-ethyl acetic acid.

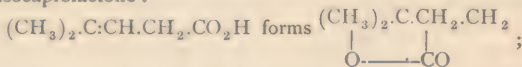
3. **Allyl-acetic Acid**,  $\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{CH}(\text{CH}_2\text{CO}_2\text{H})$ , obtained from allyl acetate and allyl malonic acid (p. 169), is an oil, smelling like valeric acid, and boiling at  $188^{\circ}$ . Nitric acid oxidizes it to succinic acid. It unites with concentrated hydrobromic acid, and forms  $\gamma$ -bromvaleric acid (a non-solidifying oil), which, upon heating with water, parts with HBr and yields the lactone of  $\gamma$ -oxyvaleric acid (see Lactones).

4. **Propylidene Acetic Acid**,  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}(\text{CO}_2\text{H}))_2$ , is obtained from propylidene malonic acid,  $\text{C}_3\text{H}_5:\text{C}(\text{CO}_2\text{H})_2$  (p. 190), and boils at  $196^{\circ}$  (*Ann.*, **218**, 160).

Tetramethylene carboxylic acid (see this) is isomeric with these unsaturated acids.

The following higher, unsaturated acids, may also be mentioned. Little is known concerning their constitution. They frequently sustain molecular transpositions:—

**Pyroterebic Acid**,  $C_6H_{10}O_2 = (CH_3)_2.C:CH.CH_2.CO_2H$ , is formed in small quantity (together with the isomeric lactone of  $\gamma$ -oxy-isocaproic acid (see this), in the distillation of terebic acid,  $C_7H_{10}O_4$  (*Annalen*, 208, 39 and 119). It is an oil which does not solidify at  $-15^\circ$ . The *calcium salt*,  $(C_6H_9O_2)_2Ca + 3H_2O$ , crystallizes in shining prisms. Protracted boiling causes the free acid to change to isomeric isocaprolactone:—



concentrated hydrobromic acid effects the same change.

**Teracrylic Acid**,  $C_7H_{12}O_2 = C_3H_7.CH:CH.CH_2.CO_2H$ , is obtained by the distillation of terpenic acid,  $C_8H_{12}O_4$  (see this), just as pyroterebic acid is formed from terebic acid. An oily liquid, with an odor resembling that of valeric acid, and boiling at  $218^\circ$  without decomposition.  $HBr$  converts it into the isomeric lactone of  $\gamma$ -oxyheptoic acid,  $C_7H_{12}(OH)O_2$ .

**Undecylenic Acid**,  $C_{11}H_{20}O_2$ , is produced by distilling castor oil under reduced pressure, when the ricinoleic acid,  $C_{18}H_{34}O_3$  (p. 196), present as a glyceride, breaks up into cenanthol,  $C_7H_{14}O$ , and undecylenic acid. It melts at  $24.5^\circ$ , and boils with partial decomposition at  $275^\circ$ . It distils unchanged under reduced pressure. When fused with caustic potash, it splits up into acetic and nonoic acid,  $C_9H_{18}O$ . Hence its structure corresponds to the formula,  $C_8H_{17}.CH:CH.CO_2H$ .

**Hypogæic Acid**,  $C_{16}H_{30}O_2$ , found as glycerol ester in earthnut oil (from the fruit of *Arachis hypogæa*), crystallizes in needles, and melts at  $33^\circ$ . Nitrous acid converts it into an isomeric modification—*gæidinic acid*, melting at  $38^\circ$ .

**Oleic Acid**,  $C_{18}H_{34}O_2$ , occurs as glycerol ester (triolein) in nearly all fats, especially in the oils, as olive oil, almond oil, cod-liver oil, etc. It is obtained in large quantities as a by-product in the manufacture of stearin candles.

In preparing oleic acid, olive or mandel oil is saponified with potash and the aqueous solution of the potassium salts precipitated with sugar of lead. The lead salts which separate are dried and extracted with ether, when lead oleate dissolves, leaving as insoluble lead palmitate, stearate and the salts of all other fatty acids. Mix the ethereal solution with hydrochloric acid, filter off the lead chloride, and concentrate the liquid. To purify the acid obtained in this way, dissolve it in ammonium hydrate, precipitate with barium chloride, crystallize the barium salt from alcohol, and decompose it away from the air by means of tartaric acid.

Oleic acid is a colorless oil, which crystallizes on cooling. It melts at  $+14^\circ$ . In a pure condition it is odorless, and does not redden litmus. On exposure to the air it oxidizes, becomes yellow and acquires a rancid odor. On fusion with caustic potash it splits up into palmitic and acetic acids. Nitric acid oxidizes it with formation of all the lower fatty acids from capric to acetic, and at the same time dibasic acids, like sebasic acid, are produced. The oleates are very similar to the salts of the fatty acids. Much water decomposes them. The solubility of the lead salt,  $(C_{18}H_{33}O_2)_2Pb$ , in ether is characteristic.

When heated to  $200^{\circ}$  with hydriodic acid and phosphorus oleic changes to stearic acid,  $C_{18}H_{36}O_2$ . It unites with bromine to form liquid dibromostearic acid,  $C_{18}H_{34}Br_2O_2$ , which is converted by alcoholic KOH into *monobromoleic acid*,  $C_{18}H_{33}BrO_2$ , and then into stearoleic acid.

Nitrous acid changes oleic into the isomeric crystalline

**Elaidic Acid**,  $C_{18}H_{34}O_2$ . This consists of brilliant leaflets, melting at  $44^{\circ}$ – $45^{\circ}$ . If fused with potash it decomposes into propionic and acetic acids. Hydriodic acid and phosphorus convert it into stearic acid. With bromine it yields the bromide,  $C_{18}H_{34}Br_2O_2$ , which melts at  $27^{\circ}$ , and when acted upon with sodium amalgam, passes back into elaidic acid.

**Erucic Acid**,  $C_{22}H_{42}O_2$ , is present as glyceride in rape-seed oil (from *Brassica campestris*) and in the fatty oil of mustard. For its preparation, rape-seed oil is saponified with lead oxide, and the lead erucate removed with ether. Erucic acid crystallizes from alcohol in long needles, which melt at  $33^{\circ}$ – $34^{\circ}$ . It forms a *dibromide*,  $C_{22}H_{42}Br_2O_2$ , with bromine. This crystallizes in warty masses, melting at  $42^{\circ}$ , and when acted upon with alcoholic potash, changes to brom-erucic acid, melting at  $33^{\circ}$ .

Hot nitric acid converts erucic acid into isomeric *brassicidic acid*, melting at  $56^{\circ}$ .

Linoleic and ricinoleic acids, although not belonging to the same series, yet closely resemble oleic acid. The first is a simple, unsaturated acid, the second an unsaturated oxy-acid.

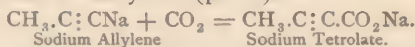
**Linoleic Acid**,  $C_{18}H_{32}O_2$ , occurs as glyceride in *drying oils* (see glycerol), such as linseed oil, hemp oil, poppy oil and nut oil. In the *non-drying* oils we have the oleic-glycerol ester. To prepare linoleic acid, saponify linseed oil with potash, precipitate the aqueous solution of the potassium salt with calcium chloride and dissolve out calcium linoleate with ether. Linoleic acid is a yellowish oil that has a specific gravity of 0.9206. It is not altered by nitrous acid.

**Ricinoleic Acid**,  $C_{18}H_{34}O_3$ , is present in castor oil, in the form of a glyceride. It is a colorless oil which solidifies at  $0^{\circ}$ . It does not alter on exposure to the air. The lead salt is soluble in ether. Subjected to dry distillation ricinoleic acid splits into œnanthol,  $C_7H_{14}O$ , and undecylenic acid,  $C_{11}H_{20}O_2$ . Fused with caustic potash it changes to sebacic acid,  $C_{18}H_{36}(CO_2H)_2$ , and secondary octyl alcohol,  $\begin{matrix} C_6H_{13} \\ CH_3 \end{matrix} \rangle CH.OH$ . It combines with bromine to a solid *dibromide*. When heated with HI (iodine and phosphorus) it is transformed into iodostearidic acid,  $C_{18}H_{33}IO_2$ , which yields stearic acid when treated with zinc and hydrochloric acid. Nitrous acid converts ricinoleic acid into isomeric *ricinelaïdic acid*. This melts at  $50^{\circ}C$ .

UNSATURATED ACIDS,  $C_nH_{2n-4}O_2$ .

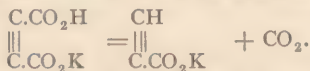
## PROPIOLIC ACID SERIES.

The members of this series have four hydrogen atoms less than the normal acids. They can be obtained from the acids of the acrylic series by treating the halogen derivatives of the latter with alcoholic potash—just as the acetylenes are produced from the olefines (see p. 61). Thus tetrolic acid,  $C_4H_4O_2$ , is obtained from the bromide of crotonic acid,  $C_4H_5BrO_2$ , and from bromcrotonic acid,  $C_4H_5BrO_2$ . They must be viewed as acetylene derivatives, formed by the replacement of one hydrogen atom by carboxyl; consequently they can be obtained by letting  $CO_2$  act upon the sodium compounds of acetylene (p. 62):—



Like the acetylenes they are capable of directly binding 2 and 4 affinities. From their structure they may contain one triple union or two double unions of two carbon atoms (see p. 60).

**Propiolic Acid**  $C_3H_2O_2 = CH : C.CO_2H$ , **Propargylic Acid** (p. 104), corresponds to propargyl alcohol. The *potassium salt*,  $C_3HKO_2 + H_2O$ , is produced from the primary potassium salt of acetylene dicarboxylic acid, when its aqueous solution is heated:—



Acetic acid results in like manner from malonic acid (p. 169).

The aqueous solution of the salt is precipitated by ammoniacal silver and cuprous chloride solutions, with formation of explosive metallic derivatives.

Free propiolic acid, liberated from the potassium salt, is a liquid with an odor resembling that of glacial acetic acid. When cool it solidifies to silky needles which melt at  $+6^\circ$ . The acid dissolves readily in water, alcohol and ether, boils with decomposition at  $44^\circ$  and reduces silver and platinum salts. Sodium amalgam converts it into propionic acid. It forms  $\beta$ -halogen acrylic acids with the halogen acids and with bromine yields dibromacrylic acid. The *ethyl ester* boils at  $118^\circ$ . When the potassium salt is boiled with water it breaks up into acetylene and a carbonate (*Ber.*, 15, 2698).

The chlor- and brom-propiolic acids ( $C_3HClO_2$  and  $C_3HBrO_2$ ) are obtained, as barium salts, from dichloracrylic acid,  $C_3H_2Cl_2O_2$ , and mucobromic acid,  $C_4H_2Br_2O_3$ . Both acids decompose readily, giving up chlor and brom-acetylene,  $C_2HBr$ .

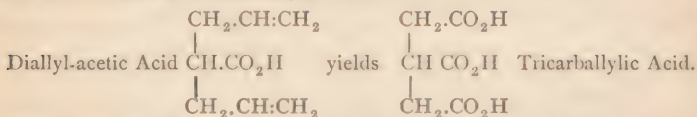
**Tetrolic Acid**,  $C_4H_4O_2 = CH_3.C : C.CO_2H$ , is obtained from  $\beta$ -chlorcrotonic acid and  $\beta$ -chlorisocrotonic acid (p. 193) when these are boiled with potash (*Annalen*, 219, 346); from sodium allylene by the action of  $CO_2$  (see above), and from the chloride of allylene by means of Na and  $CO_2$ . The acid consists



of tables, very readily soluble in water, alcohol and ether. It melts at  $76^{\circ}$  and boils at  $203^{\circ}$ . At  $200^{\circ}$  the acid decomposes into  $\text{CO}_2$  and allylene,  $\text{C}_3\text{H}_4$ . Potassium permanganate oxidizes it to acetic and oxalic acids. It combines with  $\text{HCl}$  and forms  $\beta$ -chlorcrotonic acid.

**Sorbic Acid**,  $\text{C}_6\text{H}_8\text{O}_2 = \text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$ , occurs together with malic acid in the juice of unripe mountain-ash berries (from *Sorbus aucuparia*). Liberated from its salts by distillation with sulphuric acid (*Ann.*, **110**, 129) it is an oil which does not solidify until after it has been heated with potash. In water it is almost insoluble, but crystallizes from alcohol in long needles, melting at  $134.5^{\circ}$ , and distilling at  $228^{\circ}$  without decomposition. It combines with bromine and yields the bromides,  $\text{C}_6\text{H}_8\text{Br}_2\text{O}_2$  and  $\text{C}_6\text{H}_8\text{Br}_4\text{O}_2$ —the first melting at  $95^{\circ}$  and the second at  $183^{\circ}$ . The *ethyl ester* boils at  $195^{\circ}$ . Nascent hydrogen converts the acid into *hydrosorbic acid*,  $\text{C}_6\text{H}_{10}\text{O}_2$ . This possesses an odor like that of perspiration, boils at  $208^{\circ}$ , and, when fused with  $\text{KOH}$ , yields acetic and butyric acids.

**Diallylacetic Acid**,  $\text{C}_8\text{H}_{12}\text{O}_2 = (\text{C}_3\text{H}_5)_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , is obtained from ethyl diallyl-aceto-acetate and diallyl malonic acid. It is a liquid, boiling at  $221^{\circ}$ . Nitric acid oxidizes it to tricarballic acid:—



**Undecolic Acid**,  $\text{C}_{11}\text{H}_{20}\text{O}_2$ , is obtained from the bromide of undecylenic acid (p. 195). It fuses at  $59.5^{\circ}$ . **Palmitic Acid**,  $\text{C}_{16}\text{H}_{32}\text{O}_2$ , isomeric with linoleic acid (p. 196), is obtained from the bromide of hypogaeic acid and gaidinic acid (p. 195). It melts at  $42^{\circ}$ . **Stearoleic Acid**,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ , is obtained from oleic and elaidic acids. It melts at  $48^{\circ}$ . **Behenolic Acid**,  $\text{C}_{22}\text{H}_{42}\text{O}_2$ , from the bromides of erucic and brassidic acids, melts at  $57.5^{\circ}$ . On warming the last three acids with fuming nitric acid they absorb 3 atoms of oxygen in a very peculiar manner, and afford the monobasic acids: palmitoxylic,  $\text{C}_{16}\text{H}_{38}\text{O}_4$ , stearoxylic,  $\text{C}_{18}\text{H}_{40}\text{O}_4$ , and behenoxyllic,  $\text{C}_{22}\text{H}_{46}\text{O}_4$ , which melt at  $67^{\circ}$ ,  $86^{\circ}$  and  $96^{\circ}$ , respectively.

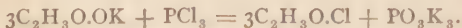
## THE ACID HALOIDS.

The haloid anhydrides of the acids (or acid haloids) are those derivatives which arise in the replacement of the hydroxyl of acids by halogens; they are the halogen compounds of the acid radicals (p. 170). Their most common method of formation consists in letting the phosphorus haloids act upon the acids or their salts—just as the alkylogens are produced from the alcohols (p. 65).

At ordinary temperatures phosphorus pentachloride acts very energetically upon the acids:—

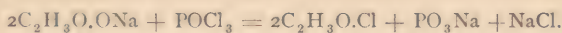


The product of the reaction is subjected to fractional distillation. It is better to have  $\text{PCl}_3$  act upon the alkali salts or the free acids; heat is then not necessary:—



By this method the pure acid chloride is at once obtained in the distillate—while the phosphite remains as residue. Or, phosphorus oxychloride (1 molecule)

may be permitted to act on the dry alkali salt (2 molecules) when a metaphosphate will remain:—

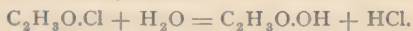


Should there be an excess of the salt, the acid will also act upon it and acid anhydrides result (p. 200).

Phosphorus bromides behave similarly. A mixture of amorphous phosphorus and bromine may be employed as a substitute for the prepared bromide (p. 67). Phosphorus iodide will not convert the acids into iodides of the acid radicals; this only occurs when the acid anhydrides are employed.

An interesting method for preparing the acid bromides consists in letting air act upon certain bromide derivatives of the alkylens, whereby oxygen will be absorbed. Thus, from  $\text{CBr}_2:\text{CH}_2$  we obtain bromacetyl bromide,  $\text{CH}_2\text{Br.COBr}$ ; from  $\text{CBr}_2:\text{CHBr}$ , dibromacetyl bromide,  $\text{CBr}_2\text{H.COBr}$  (p. 70 and *Berichte*, 12, 2247 and 13, 1980).

The acid haloids are sharp-smelling liquids, which fume in the air, because of their transformation into acids and halogen hydrides. They are heavier than water, sink in it, and at ordinary temperatures decompose, forming acids:—



The more readily soluble the resulting acid is in water, the more energetic will the reaction be.

The acid chlorides act similarly upon many other bodies. They yield compound ethers, or esters, with the alcohols or alcoholates (p. 202). With salts or acids they yield acid anhydrides (p. 200), and with ammonia, the amides of the acids, etc.

Sodium amalgam, or better, sodium and alcohol, will convert the acid chlorides into aldehydes and alcohols (pp. 91 and 149). They yield ketones and tertiary alcohols when treated with the zinc alkyls (pp. 90 and 160).

**Acetyl Chloride**,  $\text{C}_2\text{H}_3\text{OCl} = \text{CH}_3.\text{CO.Cl}$ , is produced also by the action of hydrogen chloride and phosphorus pentoxide upon acetic acid, and when chlorine acts on aldehyde. It is a colorless, pungent-smelling liquid which boils at  $55^\circ$ , and has a specific gravity of 1.130 at  $0^\circ$ . Water decomposes it very energetically.

*Preparation.*—Bring  $\text{PCl}_5$  into a retort with a tubulure, and through the latter gradually add anhydrous acetic acid. After the first violent action, apply heat and fractionate the distillate. It would be better to distil carefully a mixture of acetic acid (3 parts) and  $\text{PCl}_3$  (2 parts). Or, heat  $\text{POCl}_3$  (2 molecules) with acetic acid (3 molecules), as long as  $\text{HCl}$  escapes, then distil (*Ann.*, 175, 378). The acetyl chloride is purified by again distilling over a little dry sodium acetate.

Acetyl chloride affords the following substitution products with chlorine:  $\text{C}_2\text{H}_2\text{ClO.Cl}$ , which boils at  $106^\circ$ ;  $\text{C}_2\text{HCl}_2\text{O.Cl}$  and  $\text{C}_2\text{Cl}_3\text{O.Cl}$ , which boils at  $118^\circ$ . These are also obtained when phosphorus chloride acts on the substituted acetic acids. Monobromacetyl chloride,  $\text{C}_2\text{H}_2\text{BrO.Cl}$ , boils at  $134^\circ$ .

**Acetyl Bromide**,  $\text{C}_2\text{H}_3\text{O.Br}$ , boils at  $81^\circ$  and forms substitution products with bromine. **Monochloracetyl Bromide**,  $\text{C}_2\text{H}_2\text{ClO.Br}$ , from monochloracetic acid, boils at  $134^\circ$ .

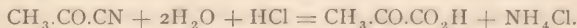
**Acetyl Iodide**,  $C_2H_3O.I$ , is obtained by letting I and P act upon acetic anhydride. It boils at  $108^\circ$  and is colored brown by separated iodine.

**Propionyl Chloride**,  $CH_3.CH_2.CO.Cl$ , boils at  $80^\circ$ ; the *bromide*,  $C_3H_5O.Br$ , at  $97^\circ$  and the *iodide*,  $C_3H_5O.I$ , at  $127^\circ$ .

**Butyryl Chloride**,  $C_4H_7O.Cl$ , from normal butyric acid, boils at  $101^\circ$ . Sodium amalgam converts it into normal butyl alcohol. **Isobutyryl Chloride**,  $(CH_3)_2.CH.CO.Cl$ , boils at  $92^\circ$ .

**Isovaleryl Chloride**,  $C_5H_9O.Cl$ , from isovaleric acid, boils at  $115^\circ$ .

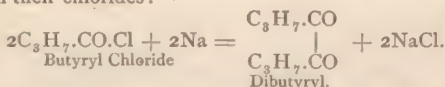
When the chlorides of the acid radicals are heated with silver cyanide, *cyanides of the acid radicals*, like acetyl cyanide,  $CH_3.CO.CN$ , result. Water or alkalis will readily convert these into their corresponding acids and hydrogen cyanide,  $CH_3.CO.CN + H_2O = CH_3.CO.OH + CNH$ . With concentrated hydrochloric acid, on the contrary, they sustain a transposition similar to that of the alkyl cyanides (p. 168), *i. e.*, carboxyl derivatives of the acid radicals—the so-called ketonic acids (see these)—are produced:—



**Acetyl Cyanide**,  $CH_3.CO.CN$ , boils at  $93^\circ$ . When preserved for some time or by the action of  $KOH$  or sodium it is transformed into a polymeric, crystalline compound,  $(C_2H_3OCN)_2$ , diacetyl cyanide. This melts at  $69^\circ$  and boils at  $208^\circ$ . Concentrated hydrochloric acid converts it into pyroracemic acid.

**Propionyl Cyanide**,  $CH_3.CH_2.CO.CN$ , from propionyl chloride, boils at  $108-110^\circ$ . **Butyryl Cyanide**,  $C_3H_7.CO.CN$ , boils at  $133-137^\circ$ ; **isobutyryl cyanide**,  $C_3H_7.CO.CN$ , at  $117-120^\circ$ . These polymerize readily to dicyanides.

The *free acid radicals*, like all monovalent groups, cannot exist free. When released from their compounds they double themselves, and may be viewed as *double ketones* or *diketones*. Sometimes this takes place when sodium or sodium amalgam acts on their chlorides:—



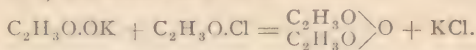
Generally this reaction is very incomplete, and the resulting diketones of the fatty series are unstable and not very characteristic (*Ber.*, 12, 315). *Dibutyryl*,  $C_3H_7.CO.CO.C_3H_7$ , is an oil, boiling at  $250^\circ$ . *Di-isovaleryl*,  $C_4H_9.CO.CO.C_4H_9$ , from isovaleryl chloride, boils with partial decomposition at  $270-285^\circ$ . The derivatives of the benzene series are more stable (see dibenzoyl).

## ACID ANHYDRIDES AND PEROXIDES.

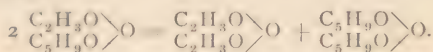
The acid anhydrides are the oxides of the acid radicals. In those of the monobasic acids two acid radicals are united by an oxygen atom; they are analogous to the oxides of the monovalent alcohol radicals—the ethers. They cannot, however, be made by the direct withdrawal of water from the acids. Anhydrides do indeed

result by the action of  $P_2O_5$ , but their quantity is very small. The following methods are employed in their preparation:—

1. The chlorides of the acid radicals are allowed to act on anhydrous salts, viz., the alkali salts of the acids:—

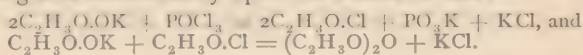


The *simple* anhydrides, those containing two *similar* radicals, can as a general thing be distilled, while the *mixed* anhydrides, with two dissimilar radicals, decompose when thus treated, into two simple anhydrides:—

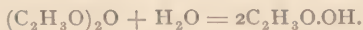


Hence they are not separated from the product of the reaction by distillation, but are dissolved out with ether.

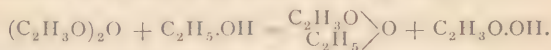
2. Phosphorus oxychloride (1 molecule) acts upon the dry alkali salts of the acids (4 molecules). The reaction is essentially the same as the first. The acid chloride which appears in the beginning acts immediately upon the excess of salt:—



The acid anhydrides are liquids or solids of neutral reaction, and are soluble in ether. Water decomposes them into their constituent acids:—



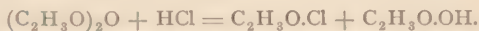
With alcohols they afford the acid esters (p. 203):—



Chlorine splits them up into acid chlorides and chlorinated acids:—



Heated with hydrochloric acid they decompose into an acid chloride and free acid:—



HBr and HI act similarly. As the *heat modulus* is positive in this reaction, the reverse reaction (action of acid chloride upon the acid) is generally not adapted to the formation of anhydrides.

**Acetic Anhydride—Acetyl Oxide**,  $(C_2H_3O)_2O$ , is a mobile liquid boiling at  $137^\circ$ . Its specific gravity equals 1.073 at  $0^\circ$ .

To prepare it, distil a mixture of anhydrous sodium acetate (3 parts) with phosphorus oxychloride (1 part); or, better, employ equal quantities of the salt



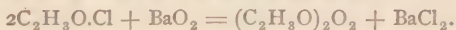
and acetyl chloride. The distillate is redistilled over sodium acetate, to entirely free it from chloride.

Nascent hydrogen converts it first into aldehyde and then into alcohol (p. 149).

**Propionic Anhydride** or **Propionyl Oxide**,  $(C_3H_5O)_2O$ , boils at  $168^\circ$ . **Butyric Anhydride**,  $(C_4H_7O)_2O$ , boils near  $190^\circ$ ; its specific gravity = 0.978 at  $12.5^\circ$ . **Isovaleric Anhydride**,  $(C_5H_9O)_2O$ , boils with partial decomposition about  $215^\circ$ . Its specific gravity at  $15^\circ$  equals 0.934. It possesses an odor like that of apples.

The higher anhydrides do not volatilize without undergoing decomposition. **Caprylic Anhydride**,  $(C_8H_{15}O)_2O$ , melts at  $0^\circ$ . **Myristic Anhydride**,  $(C_{14}H_{27}O)_2O$ , forms a fatty mass, fusing at  $54^\circ$ .

The peroxides of the acid radicals are produced on digesting the chlorides or anhydrides in ethereal solution with barium peroxide:—



**Acetyl Peroxide** is a thick liquid, insoluble in water, but readily dissolved by alcohol and ether. It is a powerful oxidizing agent, separating iodine from potassium iodide solutions and decolorizing a solution of indigo. Sunlight decomposes it, and when heated it explodes violently. With barium hydrate it yields barium acetate and barium peroxide.

## THIO-ACIDS AND THIO-ANHYDRIDES.

The thio-acids, *e. g.*, thio-acetic acid,  $CH_3.CO.SH$ , correspond to the thio-alcohols or mercaptans (p. 108), and are produced by analogous methods: by the action of acid chlorides upon potassium sulphhydrate,  $KSH$ , and by heating acids with phosphorus pentasulphide:—



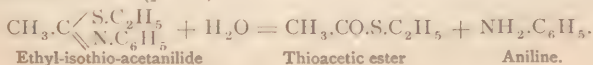
The *thio-anhydrides* arise in the same manner by the action of phosphorus sulphide upon the acid anhydrides.

The thio-acids are disagreeably smelling liquids, more insoluble in water and possessing lower boiling temperatures than the corresponding oxygen acids. Like the latter, they yield salts and esters. When heated with dilute mineral acids they break up into  $H_2S$  and fatty acids. Water slowly decomposes the thio-anhydrides into a thio-acid and an oxyacid.

The *esters* are obtained when the alkylogens react with the salts of the thio-acids, and by letting the acid chlorides act upon the mercaptans or mercaptides:—



They also appear in the decomposition of alkylic isothio-acetanilides with dilute hydrochloric acid (p. 210):—



Ethyl-isothio-acetanilide

Thioacetic ester

Aniline.

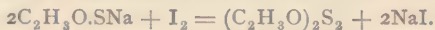
Concentrated potash resolves the esters into fatty acids and mercaptans.

**Thiacetic Acid**,  $C_2H_3O.SH$ , is a colorless liquid, boiling at  $93^\circ$ , and having a specific gravity of 1.074 at  $10^\circ$ . Its odor resembles that of acetic acid and hydrogen sulphide. It is difficultly soluble in water, but dissolves readily in alcohol and ether. The *lead salt*,  $(C_2H_3O.S)_2Pb$ , crystallizes in delicate needles, and readily decomposes with formation of lead sulphide.

**Ethyl Thiacetate**,  $C_2H_3O.S.C_2H_5$ , boils at  $115^\circ$ .

**Acetyl Sulphide**,  $(C_2H_3O)_2S$ , is a heavy, yellow liquid, insoluble in water; and is slowly decomposed by this liquid into acetic acid and thiacetic acid. It boils at  $121^\circ$ .

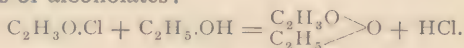
**Acetyl Disulphide**,  $(C_2H_3O)_2S_2$ , is produced when acetyl chloride acts upon potassium disulphide, or iodine upon salts of the thio-acids:—



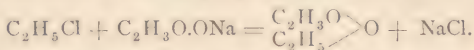
## ESTERS OF THE FATTY ACIDS.

The esters of organic acids resemble throughout those of the mineral acids (p. 113), and are prepared by analogous methods:—

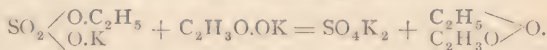
(1) By the action of acid chlorides (or acid anhydrides, p. 201) on the alcohols or alcoholates:—



(2) By the action of the alkylogens upon salts of the acids:—



(3) By the dry distillation of a mixture of the alkali salts of the fatty acids and salts of alkyl sulphates (p. 117):—



(4) By direct action of acids and alcohols, whereby water is formed at the same time:—



This transposition, as already stated, only takes place slowly (p. 114); heat hastens it, but it is never complete. If a mixture of like equivalents of alcohol and acid be employed, there will occur a time in the action when a condition of equilibrium will prevail, when the ester formation will cease, and both acid and alcohol will be simultaneously present in the mixture. This ensues, because the heat modulus of the reaction is very slight, and hence, in accordance with the principles of thermo-chemistry, and under slightly modified conditions, the reaction pursues a reverse course, *i. e.*, the ester is decomposed by more water into alcohol and acid, since heat is generated when they are dissolved by the water. Both reactions mutually limit themselves. With excess of alcohol, more acid can be changed to ester, and with excess of acid more alcohol. The formation of the esters is more complete and rapid, if the re-

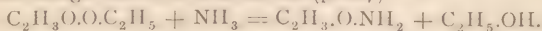
action products are assiduously withdrawn from the mixture. This may be effected either by distillation (providing the ester is readily volatilized), or by combining the water formed with sulphuric or hydrochloric acid, when the heat modulus will be appreciably augmented.\* We practically have from the above the following methods of preparation. Distil the mixture of the acid or its salt with alcohol and sulphuric acid. Or, when the esters are difficultly volatile, the acid or its salt is dissolved in excess of alcohol (or the alcohol in the acid), and while applying heat, HCl gas is conducted into the mixture (or  $\text{H}_2\text{SO}_4$  added), and the ester precipitated by the addition of water. The acid nitriles can be directly converted into esters, by dissolving them in alcohol, and heating them with dilute sulphuric acid (p. 168).

Berthelot has executed more extended investigations upon the *ester* formation. These are of great importance to chemical dynamics. He observed, for instance, that the reaction is materially accelerated by heat, but that a limit to the ester production invariably occurs, and that it equals that of the reverse transposition of the esters by water. This limiting point is independent of the speed of the reaction and temperature, but is controlled by the relative quantities, as well as the nature of the alcohol and acid. According to Berthelot the speed of the ester formation in the case of the primary normal alcohols is almost the same; the degree of the conversion or transposition equals about 66 per cent. of the mixture (with equivalent quantities of alcohol and acid). Proceeding from the simple assumption that the quantities of alcohol and acid combining in a unit of time (speed of reaction) are proportional to the product of the reacting masses, whose quantity regularly diminishes, Berthelot has proposed a formula (*Annalen, chim. phys.* 1862) by which the speed of the reaction in every moment of time and its extent can be calculated. van't Hoff has deduced a similar formula (*Berichte*, 10 669) which Guldberg-Waage and Thomsen pronounce available for all limited reactions (*ibid.* 10 1023). Of late Menschutkin has extended the investigations upon ester formations to the several homologous series of acids and alcohols (*Annalen*, 195, 334 and 197, 193, *Berichte*, 15, 1445 and 1572).

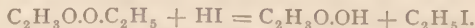
Usually the esters of fatty acids are volatile, neutral liquids, soluble in alcohol and ether, but generally insoluble in water. Heated with the latter they sustain a partial decomposition into alcohol and acid. This decomposition (*saponification*) is more rapid and complete on heating with alkalis in alcoholic solution:—



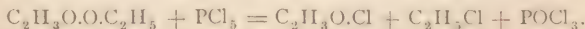
Ammonia changes the esters into amides (p. 207):—



The haloid acids convert the esters into acids and haloid-esters (*Annalen*, 211, 178):—



$\text{PCl}_5$  introduces chlorine and the radicals are converted into halogen derivatives:—




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\* Consult *Ann.*, 211, 208.

The esters of the fatty acids possess an agreeable fruity odor, are prepared in large quantities, and find extended application as *artificial fruit essences*. Nearly all fruit-odors may be made by mixing the different esters. The esters of the higher fatty acids occur in the natural varieties of wax.\*

## ESTERS OF FORMIC ACID.

**Methyl Formic Ester**,  $\text{CHO}_2\text{CH}_3$ , is obtained by distilling sodium formate with sodium methyl sulphate, or more advantageously by adding methyl alcohol (13 parts) saturated with  $\text{HCl}$ -gas to calcium formate (10 parts) and then distilling. A mobile, agreeably smelling liquid, that boils at  $32^\circ$  and has a specific gravity of 0.9984 at  $0^\circ$ . In sunlight chlorine produces **Perchlor-methyl formic ester**,  $\text{CClO}_2\text{CCl}_3$ , which boils at  $180\text{--}185^\circ$ . Its vapors conducted through a red-hot tube break up into carbonyl chloride,  $\text{C}_2\text{Cl}_4\text{O}_2 = 2\text{COCl}_2$ .

**Ethyl Formic Ester**,  $\text{CHO}_2\text{C}_2\text{H}_5$ , boils at  $54.4^\circ$  and dissolves in 10 parts water. Its specific gravity equals 0.9375. To prepare it, distil a mixture of dry sodium formate (7 parts), sulphuric acid (10 parts), and 96 per cent. alcohol (6 parts). It is better to heat a mixture of oxalic acid, glycerol and alcohol in a flask with a return cooler, until the evolution of carbon dioxide ceases, then distil off the ester; at first a glycerol ester of formic acid is produced (p. 174), which the alcohol decomposes.

The above ester serves in the manufacture of artificial rum and arrac.

The **Propyl Ester**,  $\text{CHO}_2\text{C}_3\text{H}_7$ , boils at  $81^\circ$ . **Isoamyl ester**,  $\text{CHO}_2\text{C}_5\text{H}_{11}$ , has a fruity odor and boils at  $123^\circ$ .

The **Allyl Ester**,  $\text{CHO}_2\text{C}_3\text{H}_5$ , is formed on heating oxalic acid with glycerol, and boils at  $82\text{--}83^\circ$  (p. 103).

## ESTERS OF ACETIC ACID.

The **Methyl Ester**, Methyl Acetate,  $\text{C}_2\text{H}_3\text{O}_2\text{CH}_3$ , occurs in crude wood-spirit, boils at  $57.5^\circ$ , and has a specific gravity of 0.9577 at  $0^\circ$ . When chlorine acts upon it the alcohol radical is first substituted:  $\text{C}_2\text{H}_3\text{O}_2\text{CH}_2\text{Cl}$  boils at  $150^\circ$ ;  $\text{C}_2\text{H}_3\text{O}_2\text{CHCl}_2$  boils at  $148^\circ$ .

The **Ethyl Ester**, Ethyl Acetate—Acetic Ether— $\text{C}_2\text{H}_3\text{O}_2\text{C}_2\text{H}_5$ , is a liquid with refreshing odor, and boils at  $77^\circ$ . At  $0^\circ$  its sp. gr. equals 0.9238. It dissolves in 14 parts water, and readily decomposes into acetic acid and alcohol. In preparing it, heat a mixture of 100 c.c.  $\text{H}_2\text{SO}_4$  and 100 c.c. alcohol to  $140^\circ$ , and gradually run in a mixture of 1 litre alcohol ( $95^\circ$ ) and 1 litre acetic acid (*Ber.*, 16, 1227). The distillate is shaken with a concentrated solution of salt, to withdraw all alcohol, the ether is siphoned off, dehydrated over calcium chloride, and finally rectified.

Chlorine affords substitution products of the alcohol radicals. Sodium dissolves in the anhydrous ester, forming sodium aceto-acetic ester. The **propyl ester**,  $\text{C}_2\text{H}_3\text{O}_2\text{C}_3\text{H}_7$ , boils at  $101^\circ$ ; sp. gr. 0.9091 at  $0^\circ$ . The **isopropyl ester** boils at  $91^\circ$ .

The **butyl ester**,  $\text{C}_2\text{H}_3\text{O}_2\text{C}_4\text{H}_9$ , is obtained from normal butyl alcohol. It boils at  $124^\circ$ . The ester of primary isobutyl alcohol boils at  $116^\circ$ ; that of the secondary alcohol at  $111^\circ$ , and that of the tertiary at  $96^\circ$ .

**Amyl Esters**,  $\text{C}_2\text{H}_3\text{O}_2\text{C}_5\text{H}_{11}$ . The ester of normal amyl alcohol boils at  $148^\circ$ ; that of propyl-methyl carbinol at  $133^\circ$ , and that of isopropyl-methyl carbinol at  $125^\circ$ . At  $200^\circ$  it splits up into amylene and acetic acid. The acetic ester

\* Ueber die Siedepunkte der Fettsäureester und ihre spec. Gewichte s. *Berichte*, 14, 1274 u. *Annalen*, 218, 337. Ueber die specif. Volumen. s. *Annalen*, 220, 290 u. 319.



of amyl alcohol of fermentation (p. 99) boils at  $140^{\circ}$ . A dilute alcoholic solution of it has the odor of pears and is used as *pear oil*.

*Hexyl Acetic Ester*,  $C_2H_3O_2.C_6H_{13}$ , with the normal hexyl group, occurs in the oil of *Heracleum giganteum*. It boils at  $169-170^{\circ}$  and possesses a fruit-like odor. The *octyl ester*,  $C_2H_3O_2.C_8H_{17}$ , is also present in the oil of *Heracleum giganteum*. It boils at  $207^{\circ}$  and has the odor of oranges.

The *allyl-ester*,  $C_2H_3O.O.C_3H_5$ , obtained from allyl iodide, boils at  $98-100^{\circ}$ .

### ESTERS OF PROPIONIC ACID.

The *ethyl ester*,  $C_3H_5O_2.C_2H_5$ , boils at  $98^{\circ}$ . The *propyl ester*,  $C_3H_5O_2.C_3H_7$ , boils at  $122^{\circ}$ ; the *isobutyl ester*,  $C_3H_5O_2.C_4H_9$ , at  $137^{\circ}$ ; and the *isoamyl ester*,  $C_3H_5O_2.C_5H_{11}$ , at  $160^{\circ}$ ; the latter has an odor like that of pine-apples.

### ESTERS OF THE BUTYRIC ACIDS.

**Methyl Butyric Ester**,  $C_4H_7O_2.CH_3$ , boils at  $102^{\circ}$ . The *ethyl ester*,  $C_4H_7O_2.C_2H_5$ , boils at  $120^{\circ}$ , has a pine-apple-like odor and is employed in the manufacture of artificial rum. Its alcoholic solution is the artificial *pine-apple oil*. This is prepared on a large scale by saponifying butter with sodium hydroxide and distilling the sodium salt which is formed with alcohol and sulphuric acid.

The *normal propyl ester*,  $C_4H_7O_2.C_3H_7$ , boils at  $142.7^{\circ}$ ; the *isopropyl ester*,  $C_4H_7O_2.C_3H_7$ , at  $128^{\circ}$ . The *isobutyl ester*,  $C_4H_7O_2.C_4H_9$ , boils at  $157^{\circ}$ . The *isoamyl ester*,  $C_4H_7O_2.C_5H_{11}$ , boils at  $178^{\circ}$ , and its odor resembles that of pears. The *hexyl ester* and *octyl ester* are found in the oil obtained from various species of *Heracleum* (see above).

**Ethyl Isobutyric Ester**,  $C_4H_7O_2.C_2H_5$ , boils at  $110^{\circ}$ .

The *esters* of the higher acids, as well as those of the substituted acids, are mostly mentioned along with the latter. We may yet notice here:—

**Isoamyl Isovaleric Ester**,  $C_5H_9O_2.C_5H_{11}$ , boils at  $196^{\circ}$ , and is obtained by direct oxidation of the amyl alcohol of fermentation. Its odor is very much like that of apples, and it finds application under the name *apple oil*.

The complex esters, having high molecular weights, are solids, and cannot be distilled without suffering decomposition. Thus *cetyl acetic ester*,  $C_6H_3O_2.C_{16}H_{33}$ , melts at  $18.5^{\circ}$ ; *ethyl palmitic ester*,  $C_{16}H_{31}O_2.C_2H_5$ , at  $24^{\circ}$ ; *ethyl stearic ester*,  $C_{18}H_{35}O_2.C_2H_5$ , at  $34^{\circ}$ . These esters are prepared by dissolving the acid in alcohol or the latter in the acid and then saturating the solution with HCl (p. 204). The *esters* with high alkyls break up into olefines and fatty acids (p. 54) when distilled under pressure.

Some of the higher esters occur already formed in waxes and in spermaceti.

*Spermaceti* (*Cetaceum*, *Sperma Ceti*) occurs in the oil from peculiar cavities in the head of whales (particularly, *Physeter macrocephalus*), and upon standing and cooling it separates as a white crystalline mass, which can be purified by pressing and recrystallization from alcohol. It consists of **Cetyl Palmitic Ester**,  $C_{16}H_{31}O_2.C_{16}H_{33}$ , which crystallizes from hot alcohol in waxy, shining needles or leaflets, and melts at  $49^{\circ}$ . It volatilizes undecomposed in a vacuum. Distilled under pressure, it yields hexadecylene and palmitic acid. When boiled with caustic potash it becomes palmitic acid and cetyl alcohol.

Chinese wax is **Ceryl Cerotic Ester**,  $C_{27}H_{51}O_2 \cdot C_{27}H_{55}$ . Alcoholic potash decomposes it into cerotic acid and ceryl alcohol.

Ordinary beeswax is a mixture of cerotic acid,  $C_{27}H_{51}O_2$ , with **Myricyl Palmitic Ester**,  $C_{16}H_{31}O_2 \cdot C_{30}H_{61}$ . Boiling alcohol extracts the cerotic acid and the ester remains.

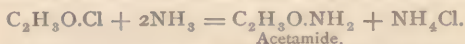
Other varieties of wax occurring in plants have been little studied.

## AMIDES.

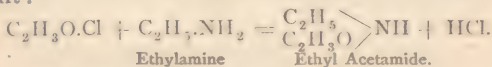
These correspond to the amines of the alcohol radicals (p. 122). The hydrogen of ammonia can be replaced by acid radicals forming primary, secondary and tertiary amides.

The following general methods for preparing primary amides are in use:—

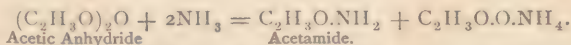
1. The action of acid chlorides upon aqueous ammonia:—



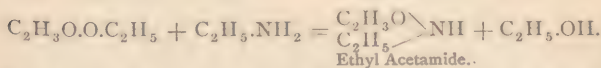
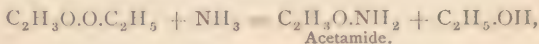
This method is especially adapted to the higher fatty acids (*Ber.*, 15, 1728). If amine bases be substituted for ammonia, mixed amides result:—



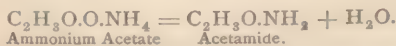
The acid anhydrides have a similar action upon ammonia and the amines:—



2. The action of ammonia and amines upon the esters—a reaction that frequently takes place in the cold; it is best, however, to apply heat to the alcoholic solution:—

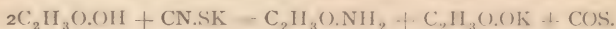


3. The dry distillation of the ammonium salts of the acids of this series. This procedure is adapted to the preparation of volatile amides. A mixture of the sodium salts and ammonium chloride may be substituted for the ammonium salts; the latter will be produced at first:—



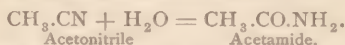
A more abundant yield is obtained by merely heating the ammonium salts to about  $230^\circ$  (*Ber.*, 15, 979).

4. The distillation of the fatty acids with potassium sulphocyanide :—



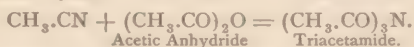
Simply heating the mixture is more practical (*Ber.*, 16, 2291 and 15, 978).

5. The addition of 1 molecule of water to the nitriles of the acids (cyanides of the alcohol radicals) :—

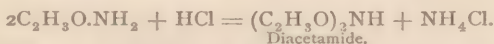


This conversion is often accomplished by acting in the cold with concentrated hydrochloric acid, or by mixing the nitrile with glacial acetic acid and concentrated sulphuric acid (*Berichte*, 10, 1061).

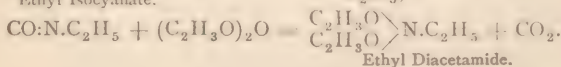
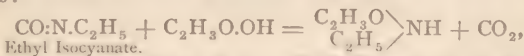
The preceding methods are not applicable in the preparation of secondary and tertiary amides, as the acid chlorides do not generally act on the primary amides. They are obtained by heating the alkyl cyanides (the nitriles) with acids, or acid anhydrides, to 200° :—



The secondary amides can also be prepared by heating primary amides with dry hydrogen chloride :—



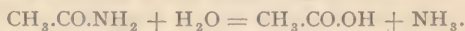
Mixed amides, which at the same time contain alcohol radicals, are further produced by the action of esters of ordinary isocyanic acid upon acids or acid anhydrides :—



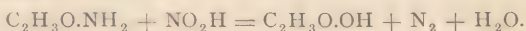
The amides of the fatty acids are usually solid, crystalline bodies, soluble in both alcohol and ether. The lower members are also soluble in water, and can be distilled without decomposition. As they contain the basic amido-group they are able to unite directly with acids, forming salt-like derivatives (*e. g.*,  $\text{C}_2\text{H}_3\text{O.NH}_2.\text{NO}_3\text{H}$ ), but these are not very stable, because the basic character of the amido-group is strongly neutralized by the acid radical. Furthermore, the acid radical imparts to the  $\text{NH}_2$ -group the power of exchanging a hydrogen atom with metals not very basic, forming metallic derivatives, *e. g.*,  $(\text{CH}_3.\text{CO.NH})_2.\text{Hg}$ —mercury acetamide, analogous to the isocyanates (from isocyanic acid,  $\text{CO:NH}$ ).

The union of the amido-group with the acid radicals (the group

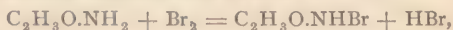
CO) is very feeble in comparison with its union with the alkyls in the amines (p. 122). The amides, therefore, readily decompose into their components. Heating with water effects this, although it is more easily accomplished by boiling with alkalies or acids:—



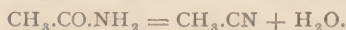
Nitrous acid decomposes the primary amides similarly (p. 125), whereby the ammonia breaks up with the evolution of nitrogen and the formation of water:—



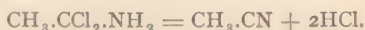
Bromine in alkaline solution changes the primary amides to brom-amides (*Ber.*, 15, 407 and 752):—



which then form amines (p. 125). On heating with phosphorus pentoxide, or with the chloride, they part with 1 molecule of water and become nitriles (cyanides of the alcohol radicals):—



In this action a replacement of an oxygen atom by two chlorine atoms takes place; the resulting chlorides, like  $\text{CH}_3\cdot\text{CCl}_2\cdot\text{NH}_2$ , then lose, upon further heating, 2 molecules of  $\text{HCl}$  with the formation of nitriles:—



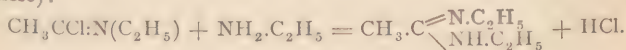
In the mixed amides, containing an alcohol radical besides the acid radical in the amido-group,  $\text{PCl}_5$  effects a similar substitution of  $2\text{Cl}$  for an oxygen atom. The products are the so-called *amid-chlorides*, which readily part with  $\text{HCl}$  and become *imid-chlorides*:—



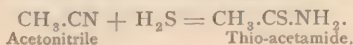
These regenerate the amides with water:— $\text{CH}_3\cdot\text{CCl}\cdot\text{N}(\text{C}_2\text{H}_5) + \text{H}_2\text{O} = \text{CH}_3\cdot\text{CO}\cdot\text{NH}(\text{C}_2\text{H}_5) + \text{HCl}$ . When heated they lose, however, hydrochloric acid and yield chlorinated bases:—



Ammonia or amines will convert the imid-chlorides into the so-called *amidines* (see these):—



Thio amides of the acids, *e. g.*, thio-acetamide,  $\text{CH}_3\cdot\text{CS}\cdot\text{NH}_2$ , and thio-benzamide,  $\text{C}_6\text{H}_5\cdot\text{CS}\cdot\text{NH}_2$ , are formed by letting phosphorus sulphide act upon the acid amides (p. 202), and by the addition of  $\text{H}_2\text{S}$  to the nitriles:—

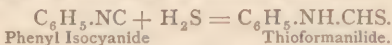


Acetonitrile

Thio-acetamide.

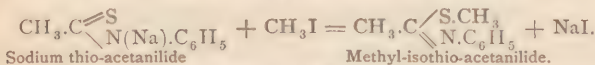


Phenyl thio-amides, in which the H of the amido-group is replaced by  $C_6H_5$ , e.g., thio-acetanilide,  $CH_3.CS.NH.C_6H_5$ , are obtained from the anilides (see these) by the action of  $P_2S_5$ ; also by acting with  $H_2S$  upon the amid-chlorides, imid-chlorides, and amidines, and by treating the latter with  $CS_2$  (*Ber.*, **11**, 506). The thio-anilides of formic acid, *thio-formanilides*, result by the addition of  $H_2S$  to the isonitriles or isocyanides (of the benzene series):—



The thio-amides resemble the amides and are readily broken up into fatty acids,  $SH_2$ ,  $NH_3$  and amines. They manifest more of an acid character than the oxygen amides, dissolve in alkalis, and readily afford metallic derivatives by the replacement of 1 hydrogen atom of the amido-group.

When iodides of the hydrocarbons act on the sodium compound of thio-acetanilide, iso-thio-acetanilides containing alcohol radicals result:—

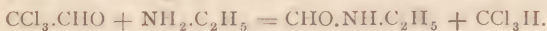


These are viewed as derivatives of the so-called isothio-acetamide,  $CH_3.C \begin{array}{c} \text{S} \\ \text{//} \\ \text{NH} \end{array}$ . The latter compound has not as yet been obtained free; it is isomeric with thio-acetamide (*Ber.*, **12**, 1062 and **16**, 144). Hydrochloric acid converts the iso-compounds having alcohol radical groups, into aniline and esters of thio-acetic acid (p. 202).

The so-called imido-thio-ethers (see these) possess a constitution like the isothio-amides.

**Formamide**,  $CHO.NH_2$ , the amide of formic acid, is obtained by heating ammonium formate to  $230^\circ$ , or ethyl formic ester with alcoholic ammonia to  $100^\circ$  (*Ber.*, **15**, 980); also by boiling formic acid with ammonium sulphocyanide (*Ber.*, **16**, 2291). It is a liquid, readily soluble in water and alcohol, and boils with partial decomposition at  $200^\circ$ . Heated rapidly, it breaks up into CO and  $NH_3$ ;  $P_2O_5$  liberates HCN from it.

**Ethyl formamide**,  $CHO.NH.C_2H_5$ , is obtained from ethyl formic ester and ethylamine; also by distilling a mixture of the latter with chloral:—



It boils at  $199^\circ$ .

**Acetamide**,  $C_2H_3O.NH_2$ , is produced on heating a mixture of dry sodium acetate and ammonium chloride, or by digesting acetic ester with alcoholic ammonia (*Ber.*, **15**, 980). It crystallizes in long needles, melts at  $82-83^\circ$ , and boils at  $222^\circ$  undecomposed. It dissolves with ease in water and alcohol, and when boiled with alkalis or acids, passes into acetic acid and ammonia. With acids, it affords unstable compounds, like  $C_2H_5NO.NO_3H$  and  $(C_2H_5NO)_2.HCl$ . When the aqueous solution is boiled with mercuric oxide, the latter dissolves, and on cooling *mercury acetamide*,  $(C_2H_3O.NH)_2Hg$ , separates (p. 208).

*Acetbromamide*,  $C_2H_3O.NHBr$  (p. 209), crystallizes from water and ether with 1 molecule  $H_2O$ , in large plates, and melts in an anhydrous condition at  $108^\circ$ .

Substituted acetamides are derived from substituted acetic esters by the action of alcoholic ammonia, and evaporation at ordinary temperatures. *Chloracetamide*,  $C_2H_2ClO.NH_2$ , melts at  $116^\circ$ , and boils at  $224-225^\circ$ . *Dichloracetamide*,  $C_2HCl_2O.NH_2$ , melts at  $96^\circ$ , and boils at  $233-234^\circ$ . *Trichloracetamide* melts at  $136^\circ$ , and boils at  $238-239^\circ$ .

*Diacetamide*,  $(C_2H_3O)_2NH$ , is obtained by heating acetamide in a stream of  $HCl$  (p. 208), is readily soluble in water, fuses at  $59^\circ$ , and boils at  $210-215^\circ$ .

*Triacetamide*,  $(C_2H_3O)_3N$ , is prepared by heating acetonitrile (methyl cyanide) with acetic anhydride to  $200^\circ$  (p. 208). It melts at  $78-79^\circ$ .

*Propionamide*,  $C_3H_5O.NH_2$ , is similar to acetamide, melts at  $75^\circ$  and boils at  $210^\circ$ .

*Butyramide*,  $C_4H_7O.NH_2$ , crystallizes in leaflets, fusing at  $115^\circ$  and boiling at  $216^\circ$ . *Isobutyramide* fuses at  $129^\circ$ .

*Isovaleramide*,  $C_5H_9O.NH_2$ , from valeric acid, sublimes in leaflets, soluble in water and fusing at  $126^\circ$ .

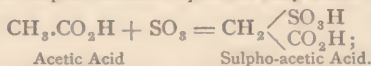
*Lauramide*,  $C_{12}H_{23}O.NH_2$ , fuses at  $102^\circ$ ; *Myristamide*,  $C_{14}H_{27}O.NH_2$ , at  $104^\circ$ ; *Palmitamide*,  $C_{16}H_{31}O.NH_2$ , at  $107^\circ$ ; *Stearamide*,  $C_{18}H_{35}O.NH_2$ , at  $109^\circ$ ; (*Berichte*, 15, 984 and 15, 1728). These higher amides may also be prepared by saponifying the fats with alcoholic ammonia, when the glycerol esters will react, just as do the esters of the monohydric alcohols.

#### CYAN-, SULPHO- AND AMIDO- DERIVATIVES OF THE ACIDS.

In the acids, the hydrogen of the acid radicals can be substituted, just as in the hydrocarbons, by the monovalent groups,  $SO_3H$ , sulpho-,  $CN$ , cyan-,  $NH_2$ , amido-, etc. The resulting derivatives having two side groups belong already to the divalent compounds and are in part described with the divalent alcohols and acids, for the preparation of which they serve as transition stages. Here we will merely call attention to the ordinary methods used in their production:—

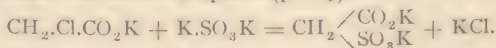
The **Sulpho-derivatives** of the monobasic acids correspond perfectly to the sulpho-compounds of the alcohol radicals (p. 119), and are obtained according to similar methods:—

(1) By the action of sulphur trioxide upon the fatty acids:—

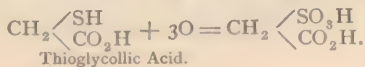


or by acting with fuming sulphuric acid on the nitriles, or amides of the acids, in which case the latter first change to acids.

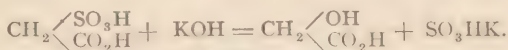
(2) By heating concentrated aqueous solutions of the salts of the monosubstituted fatty acids with alkaline sulphites (p. 119):—



(3) By oxidizing the thio-acids corresponding to the oxy-acids with nitric acid:—



The formulas indicate these sulpho-acids to be dibasic (mixed carboxylic and sulpho-acids). They correspond to the dicarboxylic acids, like  $\text{CH}_2 \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$ —malonic acid. They are mostly crystalline substances, easily soluble in water and deliquescent in the air. Their salts generally crystallize well. The sulpho-group in them is not so intimately combined as in the sulphonic acids of the alcohol radicals. Boiling alkalis convert them into oxy-acids:—



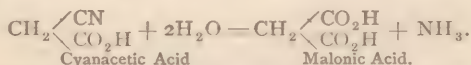
**Sulpho-acetic Acid**,  $\text{CH}_2 \begin{smallmatrix} \text{SO}_2\text{OH} \\ \text{CO}_2\text{H} \end{smallmatrix}$ , is obtained by oxidizing isothionic acid,  $\text{CH}_2(\text{OH}).\text{CH}_2.\text{SO}_3\text{H}$ , with nitric acid. Sulphuric acid liberates it from its readily soluble barium salt. The acid crystallizes with  $1\frac{1}{2}$  molecules  $\text{H}_2\text{O}$  in deliquescent prisms, which fuse at  $70^\circ$ . The barium salt,  $\text{CH}_2 \begin{smallmatrix} \text{SO}_3 \\ \text{CO}_2 \end{smallmatrix} \text{Ba} + \text{H}_2\text{O}$ , forms leaflets. Pentachloride of phosphorus converts it into the chloride,  $\text{CH}_2 \begin{smallmatrix} \text{SO}_2\text{Cl} \\ \text{CO}_2\text{Cl} \end{smallmatrix}$ . By reduction of the latter with tin and hydrochloric acid thio-glycollic acid,  $\text{CH}_2 \begin{smallmatrix} \text{SH} \\ \text{CO}_2\text{H} \end{smallmatrix}$ , is produced.

The sulpho-derivatives of the higher acids of the marsh-gas series have not been well studied.

The **Cyan-derivatives** are obtained by heating the monohalogen acids (their salts or esters) with aqueous or alcoholic potassium cyanide:—



As a usual thing they crystallize poorly and are unstable. When boiled with alkalis or acids they are converted into dibasic acids (p. 168):—



**Cyanformic Acid**,  $\text{CN.CO}_2\text{H}$ . In the following pages this will be considered as *cyanacetic acid*.

**Cyanacetic Acid**,  $\text{CH}_2(\text{CN}).\text{CO}_2\text{H}$ , is derived from monochlor-malonic acid. It is a crystalline mass, readily soluble in water, melting at  $80^\circ$ , and about  $165^\circ$  splitting up into  $\text{CO}_2$  and acetonitrile,  $\text{CH}_3.\text{CN}$ . Malonic acid is produced when it is boiled with alkalis or acids.

*Preparation.*—Boil monochloracetic ester (5 parts) with potassium cyanide (6 parts) and water (24 parts), or alcohol, until the odor of prussic acid has disappeared, then neutralize the solution with  $\text{H}_2\text{SO}_4$ , concentrate, supersaturate with sulphuric acid and withdraw the cyanacetic acid by shaking the liquid with ether.

*α*-Cyanpropionic Acid,  $\text{CH}_3\text{CH}(\text{CN})\text{CO}_2\text{H}$ , from *α*-chloropropionic acid, yields isosuccinic acid. *β*-Cyanpropionic Acid,  $\text{CH}_3\text{CH}_2\text{CN}\text{CO}_2\text{H}$ , yields ordinary succinic acid.

The amido-acids, such as amido-acetic acid,  $\text{CH}_2(\text{NH}_2)\text{CO}_2\text{H}$ , will be treated along with the divalent oxy-acids (lactic acid series), where their relations will be more manifest.

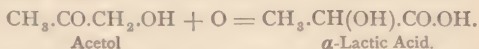
At this point we will introduce the *ketone alcohols* and *ketonic acids*, as they constitute the transition to the divalent alcohols and acids. As we have already observed, the various families of chemical substances are characterized by particular atomic groups—the alcohols by the hydroxyl group, OH, the aldehydes by the aldehyde group, CHO, the ketones by the group CO, the acids by the carboxyl group,  $\text{CO}_2\text{H}$ , etc. These characterizing atomic groups can appear *simultaneously* in the same molecule, thus giving rise to the formation of compounds with *mixed function*—aldehyde alcohols, aldehyde acids, ketone alcohols, ketonic acids, etc. These derivatives exhibit at the same time the specific properties of various classes of compounds.

## KETONE ALCOHOLS.

1. **Acetyl Carbinol, Acetol**,  $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{OH}$ , is only known in aqueous solution. It is obtained from monobromacetone by the action of silver oxide or potassium carbonate, and by fusing cane and grape sugar with caustic alkali (*Berichte*, 16, 837). Acetol, its ethyl ether, and its esters may be formed from the corresponding propargylic compounds by hydration with  $\text{HgBr}_2$  (p. 61):—



Its solution reduces alkaline copper solutions even in the cold (p. 150). The *ethyl ether*,  $\text{C}_3\text{H}_5\text{O}\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , boils at  $128^\circ$ . The *acetyl ester*,  $\text{C}_3\text{H}_5\text{O}\cdot\text{O}\cdot\text{C}_2\text{H}_3\text{O}$ , is obtained from chloracetone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , by heating the latter with potassium acetate and alcohol. It boils at  $172^\circ$ ; has a specific gravity = 1.053 at  $11^\circ$ , and is readily soluble in water. The *benzoyl ester*,  $\text{C}_3\text{H}_5\text{O}\cdot\text{O}\cdot\text{C}_7\text{H}_5\text{O}$ , melts at  $24^\circ$ . The esters reduce alkaline copper solutions when heated, forming *α*-lactic acid (*Berichte*, 13, 2344):—



Acetol

*α*-Lactic Acid.

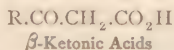
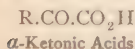
2. **Diacetone Alcohol**,  $\text{C}_6\text{H}_{12}\text{O}_2 = \text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\text{OH}$ , is obtained from diacetoneamine (p. 166) by the action of nitrous acid. A liquid, miscible with water, alcohol and ether. Specific gravity = 0.930 at  $25^\circ$ . It boils at  $164^\circ$ . Mixed with sulphuric acid it parts with water and becomes mesityl oxide (p. 165).

The aldehyde alcohols, such as glycol aldehyde,  $\text{CH}_2\cdot\text{OH}\cdot\text{CHO}$ , and aldol, and the aldehyde acids, like glyoxylic acid,  $\text{CHO}\cdot\text{CO}_2\text{H}$ , will be described together with the divalent alcohols and acids.

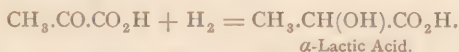


## KETONIC ACIDS.

These contain both the groups CO and CO<sub>2</sub>H; they, therefore, show acid and ketone characters with all the specific properties peculiar to these (p. 213). In conformity with the manner of designating the mono- and di-substituted fatty acids (pp. 179 and 180), we distinguish the groups  $\alpha$ -,  $\beta$ - and  $\gamma$ - of the ketonic acids. These differ from each other by various peculiarities:—



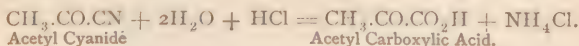
The  $\alpha$ - and  $\gamma$ -acids are tolerably stable, even in a free condition, whereas the  $\beta$ -acids are only so when in the form of esters. When they are set free from these they readily decompose (p. 216). Nascent hydrogen converts all the ketonic acids into the corresponding divalent oxy-acids. In this change the ketone group becomes a secondary alcohol group:—



They unite with alkaline sulphites (in accord with their ketone nature) to form crystalline compounds, from which alkalies or acids again set them free.

### 1. $\alpha$ -Ketonic Acids—R.CO.CO<sub>2</sub>H.

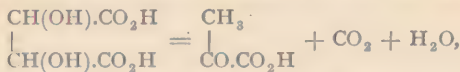
In this class the ketone group CO is in direct union with the acid-forming carboxyl group, CO<sub>2</sub>H. We can view them as compounds of acid radicals with carboxyl, or as derivatives of formic acid, HCO.OH, in which the hydrogen linked to carbon is replaced by an acid radical—hence the designation *acetyl carboxylic acid* or *acetyl formic acid* for the acid, CH<sub>3</sub>.CO.CO<sub>2</sub>H. The first name indicates, too, the general synthetic method of formation of these acids from the cyanides of acid radicals (p. 200), which, by the action of concentrated hydrochloric acid, are changed to the corresponding ketonic acids:—



Nascent hydrogen converts the  $\alpha$ -ketonic acids (their esters) into  $\alpha$ -oxyacids (see above).

(1) **Pyroracemic Acid, Pyruvic Acid** (acetyl carboxylic acid), C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> = CH<sub>3</sub>.CO.CO<sub>2</sub>H, was first obtained in the distillation of tartaric acid and glyceric acid. It is synthetically prepared from  $\alpha$ -dichloropropionic acid, CH<sub>3</sub>.CCl<sub>2</sub>.CO<sub>2</sub>H (p. 180), when heated with water and silver oxide, and from acetyl cyanide by the action of hydrochloric acid (see above).

For its preparation heat tartaric acid in an iron pan until the mass browns and swells up. After cooling, the mass is broken into pieces, placed in a retort and distilled over a free flame (*Ann.*, 172, 142). A large yield (about 60 per cent.) is reached by distilling tartaric acid with potassium bisulphate (*Berichte*, 14, 321). The formation of pyroracemic acid from tartaric acid (racemic acid and glyceric acid):—



is quite similar to the transpositions cited on page 103.

Pyroracemic acid is a liquid, soluble in alcohol, water and ether, and has an odor quite similar to that of acetic acid. It boils at 165–170°, decomposing partially into CO<sub>2</sub> and pyrotartaric acid (2C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> = C<sub>5</sub>H<sub>8</sub>O<sub>4</sub> + CO<sub>2</sub>). This conversion occurs more readily on heating with hydrochloric acid to 100°. Pyruvic acid is monobasic. Its salts crystallize with difficulty.

When the acid or its salts are heated with water, or if the acid be set free from its salts by mineral acids, it passes into a syrup-like, non-volatile mass, which, on distillation, becomes pyrotartaric acid.

Pyruvic acid forms crystalline compounds with the acid alkaline sulphites. It resembles the ketones in this respect.

Nascent hydrogen (Zn and HCl, or HI) changes it to ordinary  $\alpha$ -lactic acid, CH<sub>3</sub>.CH(OH).CO<sub>2</sub>H. PCl<sub>5</sub> converts it into the chloride of  $\alpha$ -dichloropropionic acid, CH<sub>3</sub>.CCl<sub>2</sub>.COCl (p. 180). With hydroxylamine, it yields  $\alpha$ -isonitrosopropionic acid (p. 180). It combines with CNH, like all ketone compounds, and forms an oxy-cyanide (p. 161), from which  $\alpha$ -oxyis Succinic acid is obtained. Pyruvic acid also condenses readily to benzene derivatives (p. 165). Thus, uvitic acid, C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>, results when the acid is heated with barium hydrate. Ammonia, however, produces uvitonic acid—a pyridine derivative. It readily furnishes condensation products with hydrocarbons of the benzene series (*Ber.*, 14, 1595).

It combines with bromine, forming a crystalline, unstable addition product, C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>Br<sub>2</sub>. Substitution products result by heating the acid with bromine and water to 100°; dibrom-pyruvic acid, CBr<sub>2</sub>H.CO.CO<sub>2</sub>H, crystallizes with 2H<sub>2</sub>O in large, rhombic plates. It loses its water of crystallization when exposed, and melts at 89°. Tribrom-pyruvic acid, CBr<sub>3</sub>.CO.CO<sub>2</sub>H or CBr<sub>3</sub>.C(OH)<sub>2</sub>.CO<sub>2</sub>H, is formed by heating  $\alpha$ -lactic acid with bromine and water. It has two molecules of water of crystallization, and consists of brilliant leaflets which lose water at 100°, and then fuse at 90°. When heated with water or ammonia, it breaks up into bromoform, CHBr<sub>3</sub>, and oxalic acid.

(2) **Propionyl-carboxylic Acid**, C<sub>2</sub>H<sub>5</sub>.CO.CO<sub>2</sub>H, is obtained from propionyl cyanide. It is very similar to pyruvic acid, and can only be distilled under diminished pressure. Nascent hydrogen converts it into  $\alpha$ -oxybutyric acid.

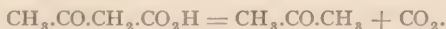
(3) **Butyryl-carboxylic Acid**, C<sub>3</sub>H<sub>7</sub>.CO.CO<sub>2</sub>H, is derived from butyryl cyanide, and boils at 180–185° with slight decomposition. It decomposes readily into CO<sub>2</sub> and butyric acid.

2.  $\beta$ -Ketonic Acids.

In the  $\beta$ -ketonic acids the ketone oxygen atom is attached to the second carbon atom, counting from the carboxyl group forward. These compounds are very unstable when free and when in the form of salts. Heat decomposes them into  $\text{CO}_2$  and ketones. Their esters, on the other hand, are very stable, can be distilled without decomposition, and serve for various and innumerable syntheses.

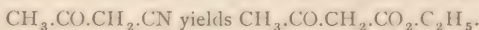
The first acid of this class is:—

**Aceto-acetic Acid**,  $\text{C}_4\text{H}_6\text{O}_3 = \text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . We can regard this as acetic acid in which an hydrogen atom of methyl is replaced by acetyl,  $\text{CH}_3\cdot\text{CO}$ , or as acetone in which carboxyl has taken the place of an hydrogen atom—hence the designation *acetone carboxylic acid*. To obtain the acid, the esters are saponified *in the cold* by dilute potash, or the barium salt is decomposed with sulphuric acid, and the solution shaken with ether (*Ber.*, **15**, 1871, **16**, 830). Concentrated over sulphuric acid, aceto-acetic acid is a thick liquid, strongly acid, and miscible with water. When heated it yields  $\text{CO}_2$  and acetone:—

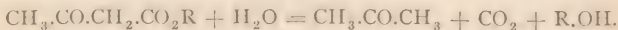


Nitrous acid converts it at once into  $\text{CO}_2$  and isonitroso-acetone (p. 163). Even its salts are only slightly stable. It is difficult to obtain them pure, and they sustain changes similar to those of the acid. Ferric chloride imparts to them, and also to the esters, a violet-red coloration. Occasionally the sodium or potassium salt is found in urine (*Ber.*, **16**, 2314).

The *ethyl ester*,  $\text{C}_3\text{H}_5\text{O}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$ , can be directly synthesized from monochloroacetone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , by converting the latter into cyanide, and treating this with  $\text{HCl}$  or alcohol (p. 168).



It can, however, be obtained (at first the sodium compound) by the action of metallic sodium upon ethyl acetic ester (below). Like the free acid, this and also other esters break up into  $\text{CO}_2$ , acetone and alcohol, when heated with alkalis:—



The esters of aceto-acetic acid, contrary to expectation, possess an *acid-like* character. They dissolve in alkalis, forming salt like compounds in which an hydrogen atom is replaced by metals. All their reactions indicate that it is the hydrogen of the  $\text{CH}_2$  (attached to two  $\text{CO}$  groups) that has the nature of an acid hydrogen. The constitution of the sodium compound (and of other salts) is expressed by the formula:—



We here observe an influence of the negative groups CO upon the hydrogen in union with carbon (in the atomic grouping CO. CH<sub>2</sub>.CO) similar to that exercised by the nitro-group in the nitro-paraffins (p. 79). The group CH<sub>2</sub> manifests the same deportment in the esters of malonic acid, CH<sub>2</sub> <  $\begin{smallmatrix} \text{CO.OH} \\ \text{CO.OH} \end{smallmatrix}$ , and in all similarly constructed derivatives, as it does in the esters of aceto-acetic acid.

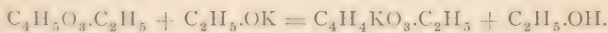
The sodium compounds of the aceto-acetic esters are the starting points in the preparation of the free esters and their derivatives. They result in the action of sodium upon acetic esters. The reaction follows (in the case of ethyl acetic ester) the equation:—



The sodium compound of methyl aceto-acetic ester is formed in a similar manner from methyl acetic ester, etc.

Acids separate the free esters from the sodium compounds. They are purified by distillation.

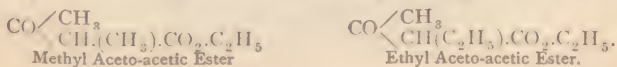
The sodium and potassium compounds are obtained pure from the aceto-acetic esters by treating the latter with potassium or sodium, or better, the alcoholates of the latter (in equivalent quantities):—



They dissolve readily in water and alcohol, react alkaline and on exposure decompose. The decomposition is more rapid on boiling with water (similar to the free aceto-acetic esters) (p. 216). Dilute acids liberate the esters. When the latter are dissolved in barium hydrate, corresponding barium compounds are formed, from which derivatives of the heavy metals are obtained by double decomposition. Ammoniacal solutions of metallic salts afford the same directly from the aceto-acetic esters (*Ann.*, 188, 268).

*Preparation of Ethyl Aceto-acetic Ester.*—60 parts metallic sodium are gradually dissolved in 2000 parts pure ethyl acetic ester. The excess of the latter is distilled off. On cooling the mass solidifies to a mixture of sodium aceto-acetic ester and sodium ethylate. The mass remaining liquid is mixed with acetic acid (50 per cent.) in slight excess. The oil separated and floating on the surface of the water is siphoned off, dehydrated with calcium chloride, and fractionated (*Ann.*, 214, and 213, 137). For the preparation of the dry sodium compound see *Ann.*, 201, 143.

Different monovalent radicals can be substituted for the metal in the sodium aceto-acetic esters. Thus by the action of the alkyl iodides (or bromides), sodium iodide separating, we get:—

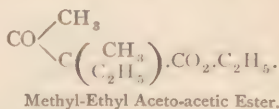
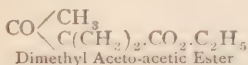




In these mono-alkylic aceto-acetic esters another hydrogen atom can be replaced by sodium by the action of the metal or sodium ethylate :—

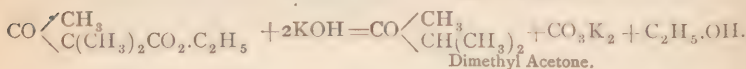
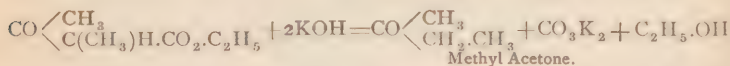


If alkyl iodides be again permitted to act upon these last derivatives, a second alkyl group may be introduced, yielding dialkyl aceto-acetic esters, *e. g.*,—

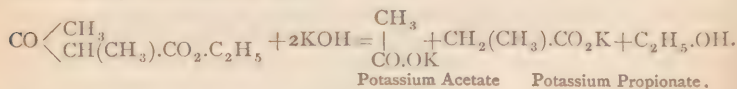


To execute these syntheses, it is not necessary to prepare pure sodium compounds. To the aceto-acetic ester dissolved in 10 times its volume of absolute alcohol, add an equivalent amount of sodium and then the alkyl iodide, after which heat is applied. To introduce a second alkyl, employ again an equivalent quantity of the sodium alcoholate and the alkyl iodide (*Annalen*, 192, 153).

On heating the mono- or dialkyl aceto-acetic esters with alkalis in *dilute* aqueous or alcoholic solution, or with barium hydrate, they decompose after the manner of aceto-acetic esters (p. 216), forming ketones (alkylic acetones):—

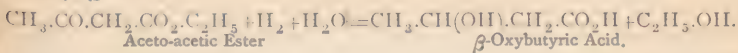


At the same time another splitting-off takes place, by which the alkyl acetic acids, *i. e.*, the higher fatty acids (p. 169) are produced along with acetic acid :—

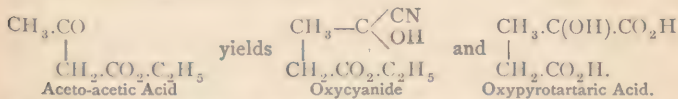


Both of these reactions, in which decomposition occurs (the splitting-off of ketone and of acid), usually take place simultaneously. In using dilute potash or caustic baryta, the ketone-decomposition predominates, whereas, with very concentrated alcoholic potash, the same may be asserted in regard to the acid-decomposition (*Annalen*, 190, 276). The splitting-off of ketone, with elimination of  $\text{CO}_2$ , occurs almost exclusively on boiling with sulphuric or hydrochloric acid (1 part acid and 2 parts water). In this case, ketones, or with the dibasic ketonic acids, ketone monocarboxylic acids are produced (*Annalen*, 216, 133). The aceto-acetic esters undergo a decomposition similar to the splitting-off of acid if they are heated alone to  $250^\circ$ , or with sodium ethylate free from alcohol, when, instead of acetic acid, we obtain *dehydracetic acid*,  $\text{C}_8\text{H}_8\text{O}_4$ .

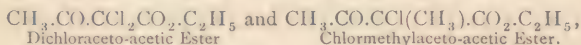
The aceto-acetic esters are changed by nascent hydrogen (sodium amalgam) into the corresponding  $\beta$ -oxy-acids (of the lactic acid series) (p. 214):—



They are saponified at the same time. As ketones, they also unite with CNH, forming oxycyanides (p. 161), which HCl converts into oxydicarboxylic acids:—



In the aceto-acetic esters, the hydrogen of the group  $\text{CO}\cdot\text{CH}_2\cdot\text{CO}$  can be directly replaced by chlorine and bromine. The products, like

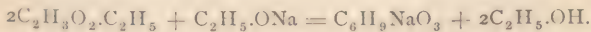


suffer changes with alkalis and acids analogous to those sustained by the aceto-acetic esters (see above). Thus, from dichloraceto-acetic esters are obtained: dichloracetone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CHCl}_2$ , and dichloracetic acid,  $\text{CHCl}_2\cdot\text{CO}_2\text{H}$ ; and from chlormethylaceto-acetic ester result chlormethyl-ethyl ketone, and  $\alpha$ -chlorpropionic acid,  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CO}_2\text{H}$ , etc.

All the aceto-acetic esters combine with hydroxylamine to form esters of the corresponding isonitroso-fatty acids (p. 171). Nitrous acid changes them to the isonitroso-derivatives,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}_2\text{R}$ , which readily break up into isonitroso-acetone and  $\text{CO}_2$  (see below). The aceto-acetic esters with one alcohol radical decompose directly into isonitroso-acetones (p. 163).

The aceto-acetic esters are capable of various other reactions, in which the group  $\text{CH}_2$  also acts a prominent part. Thus, they combine with the diazo-compounds of the benzene series, form condensation products with the aldehydes (*Annalen*, 218, 170), and like the ketones are capable of directly forming condensation modifications (*Annalen*, 222, 4).

**Ethyl Aceto-acetic Ester**,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5 = \text{C}_6\text{H}_{10}\text{O}_3$ , *Aceto-acetic Ester*, is formed by the action of sodium upon ethyl acetic ester (p. 216). It is a pleasantly smelling liquid, of sp. gr. 1.0526 at  $20^\circ$ , boils at  $180.8^\circ$  and distils over with steam. The ester is only slightly soluble in water, and has a neutral reaction (that of the methyl ester is acid). Ferric chloride colors it violet. The *sodium* compound,  $\text{C}_6\text{H}_9\text{NaO}_3$  (p. 217) crystallizes in long needles, and is made by heating ethyl acetic ester with sodium ethylate:—



The *copper salt*,  $(\text{C}_6\text{H}_9\text{O}_3)_2\text{Cu}$ , is precipitated in the form of a bright green powder.

Boiling alkalis or acids convert the ester into acetone,  $\text{CO}_2$  and

alcohol. Heated alone or with sodium ethylate to  $230-250^{\circ}$ , it yields ethyl acetic ester and dehydracetic acid:—



The constitution of **Dehydracetic Acid**,  $\text{C}_8\text{H}_8\text{O}_4$ , is not determined. It crystallizes in needles, melts at  $108^{\circ}$  and boils at  $269^{\circ}$ . It dissolves with difficulty in alcohol and water, but readily in ether. It reacts acid, combines with 1 equivalent of metal to form salts, and appears to be monobasic. An isomeric acid, *isodehydracetic acid*, is obtained by the decomposition of the condensation products of aceto-acetic ester, induced by sulphuric acid (*Ann.*, 222, 9).

Aceto-acetic ester becomes  $\beta$ -oxybutyric acid under the action of sodium amalgam. It forms an oxycyanide with  $\text{CNH}$ , from which oxypyrotartaric acid is formed (p. 219).  $\text{PCl}_5$  replaces the oxygen of the  $\text{CO}$ -group by 2 atoms of chlorine. The *chloride*,  $\text{CH}_3.\text{CCl}_2.\text{CH}_2.\text{CO.Cl}$ , readily splits off  $\text{HCl}$  and yields two chlorocrotonic acids (p. 192). Fuming nitric acid changes it to isonitrosoacetic ester (p. 178).

When chlorine is conducted into aceto-acetic ester, **Dichloraceto-acetic Ester**,  $\text{CH}_3.\text{CO.CCl}_2.\text{CO}_2.\text{C}_2\text{H}_5$ , is produced. It is a pungent-smelling liquid boiling at  $205-207^{\circ}$ . Heated with  $\text{HCl}$  it decomposes into  $\alpha$ -dichloroacetone  $\text{CH}_3.\text{CO.CHCl}_2$ , alcohol and  $\text{CO}_2$ ; with alkalis it yields acetic and dichloroacetic acids (*Berichte*, 16, 1553).  $\text{SO}_2\text{Cl}_2$  converts aceto-acetic ester into **Monochloraceto-acetic Ester**,  $\text{C}_2\text{H}_3\text{O.CHCl.CO}_2.\text{C}_2\text{H}_5$ . It boils at  $194^{\circ}$ .

Bromine replaces from 1-5 atoms of hydrogen forming esters, like  $\text{C}_2\text{H}_3\text{O.CHBr.CO}_2.\text{C}_2\text{H}_5$ , which are syrupy liquids that decompose on heating (*Ann.*, 219, 97 and *Berichte*, 16, 1553).

**Isonitroso aceto-acetic Ester**,  $\text{C}_2\text{H}_3\text{O.C(N.OH).CO}_2.\text{C}_2\text{H}_5$ , is formed on dissolving ethyl aceto-acetate in dilute potash, adding a solution of potassium nitrite (1 molecule  $\text{NO}_2\text{K}$ ) and acidifying with dilute sulphuric acid (*Berichte*, 15, 1326). Shining leaflets or prisms which melt at  $53^{\circ}$ , and decompose when heated (p. 219). It has an acid reaction, dissolves in alkalis with a yellow color and is colored an intense red by phenol and sulphuric acid (p. 79).

**Amido-aceto-acetic Ester**,  $\text{C}_2\text{H}_3\text{O.CH(NH}_2\text{).CO}_2.\text{C}_2\text{H}_5$ , is obtained by the action of dry or aqueous ammonia upon aceto-acetic ester. It melts at  $21^{\circ}$ , and boils at  $214^{\circ}$ .

**Methyl Aceto-acetic Ester**,  $\text{CH}_3.\text{CO.CH}_2.\text{CO}_2.\text{CH}_3$ , is formed from methyl acetate (p. 217). It boils at  $170^{\circ}$ , and is colored a dark cherry-red by ferric chloride. Otherwise it is perfectly similar to the ethyl ester.

**Methyl Ethyl Aceto-acetic Ester**,  $\text{CO} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{C(CH}_3\text{)H.CO}_2.\text{C}_2\text{H}_5 \end{array}$   
 $= \text{C}_7\text{H}_{12}\text{O}_3$  (p. 217), ( $\alpha$ -aceto-propionic ester). This boils at  $186^{\circ}$  and has a sp. gr. 1.01 at  $12^{\circ}$ . Potash readily decomposes it into methyl acetone,  $\text{CO}_2$  and alcohol. By the acid-decomposition it yields propionic acid. *Free* methyl aceto-acetic acid, obtained by saponification of the ester with alkalis in the cold, is very similar to aceto-acetic acid (p. 216).

**Dimethyl Aceto-acetic Ester**,  $\text{CO} \begin{smallmatrix} \text{CH}_3 \\ \diagdown \\ \text{C}(\text{CH}_3)_2 \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5 \end{smallmatrix} =$

$\text{C}_8\text{H}_{14}\text{O}_3$ , is an oil, nearly insoluble in water, of sp. gravity 0.991 at  $16^\circ$ . It boils at  $190^\circ$ . Boiling aqueous potash does not affect it. Alcoholic potash, however, or baryta water, changes it to dimethyl acetone,  $\text{CO}_2$  and alcohol. By the acid-decomposition it yields isobutyric acid,  $(\text{CH}_3)_2\text{CH} \cdot \text{CO}_2\text{H}$ . The *free* acid is crystalline, but very unstable.

**Ethyl Aceto-acetic Ester**,  $\text{CO} \begin{smallmatrix} \text{CH}_3 \\ \diagdown \\ \text{CH}(\text{C}_2\text{H}_5) \end{smallmatrix} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$ , is difficultly soluble in water. It boils at  $195^\circ$ . Its specific gravity equals 0.998 at  $6^\circ$ . Ferric chloride colors it blue. Boiled with aqueous potash, it decomposes into ethylacetone,  $\text{CO}_2$ , and alcohol. In the acid-decomposition it affords normal butyric acid.

**Diethyl Aceto-acetic Ester**,  $\text{CO} \begin{smallmatrix} \text{CH}_3 \\ \diagdown \\ \text{C}(\text{C}_2\text{H}_5)_2 \end{smallmatrix} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5 = \text{C}_{10}\text{H}_{18}\text{O}_3$ , is insoluble in water, boils at  $210\text{--}212^\circ$ , and has a specific gravity at  $0^\circ$  of 0.974. Aqueous potash has no effect upon it, while with alcoholic potash or baryta water it yields diethyl ketone,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}(\text{C}_2\text{H}_5)_2$ . By the acid-decomposition (with sodium ethylate) diethylacetic acid results. The free diethyl-aceto-acetic acid is liquid, and when distilled, yields  $\text{CO}_2$  and diethyl acetone.

**Methyl-ethyl Aceto-acetic Ester**,  $\text{CO} \begin{smallmatrix} \text{CH}_3 \\ \diagdown \\ \text{C}(\text{CH}_3)(\text{C}_2\text{H}_5) \end{smallmatrix} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5 =$   
 $\text{C}_9\text{H}_{16}\text{O}_3$ . It boils at  $198^\circ$ . By decomposition it furnishes methyl-ethyl acetone and methyl-ethyl acetic acid (p. 184).

**Allyl Aceto-acetic Ester**,  $\text{CO} \begin{smallmatrix} \text{CH}_3 \\ \diagdown \\ \text{CH}(\text{C}_3\text{H}_5) \end{smallmatrix} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5 = \text{C}_9\text{H}_{14}\text{O}_3$ , is obtained by the action of allyl iodide upon sodium aceto-acetic ester. It boils at  $206^\circ$ ; its specific gravity is 0.982 at  $17.5^\circ$ . Ferric chloride gives it a carmine-red coloration. When it decomposes, allyl acetone and allyl acetic acid are produced (p. 194). Sodium amalgam changes it into an allyloxybutyric acid. By the addition of more allyl, we obtain

**Diallyl-aceto-acetic Ester**,  $\text{CO} \begin{smallmatrix} \text{CH}_3 \\ \diagdown \\ \text{C}(\text{C}_3\text{H}_5)_2 \end{smallmatrix} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$ , which boils at  $206^\circ$ , and decomposes into diallyl acetone and diallyl acetic acid.

By the action of propyl iodide, isopropyl iodide, isobutyl iodide, amyl iodide, benzyl chloride,  $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{Cl}$ , etc., higher aceto-acetic esters have been formed, from which, by decomposition, higher ketones and fatty acids resulted, and were converted into higher oxy-acids by the addition of  $\text{H}_2$ .

The hydrogen in the aceto-acetic esters may also be replaced by *acid radicals*, by letting the latter act on the sodium compounds, suspended in ether. Thus arise the diketon-monocarboxylic esters. Acetyl chloride forms:—

**Acetyl aceto-acetic Ester**,  $\text{C}_2\text{H}_3\text{O} \cdot \text{CH}(\text{C}_2\text{H}_3\text{O}) \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$ , or **Diaceto-acetic Ester**,  $\text{CH}_3 \cdot \text{CO} \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{CH} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$ . It boils with partial decomposition at  $210^\circ$ , and when heated with water, breaks up into acetic acid, aceto acetic ester and  $\text{CO}_2$  (*Ber.* 16, 2762). **Ethyl-diaceto-acetic Ester**,  $(\text{CH}_3 \cdot \text{CO})_2 \cdot \text{C}(\text{C}_2\text{H}_5) \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$ , boils at  $235^\circ$ , is insoluble in potash, and is not colored by ferric chlo-



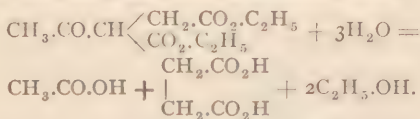
ride. **Benzoyl aceto-acetic Ester**,  $\text{CH}_3\text{CO} \begin{matrix} \text{CH}_3\text{CO} \\ \text{C}_6\text{H}_5\text{CO} \end{matrix} \text{CH.CO}_2\text{R}$ , breaks up when boiled with sulphuric acid into benzoyl acetone,  $\text{CH}_3\text{CO.CH}_2\text{CO.C}_6\text{H}_5$  (*Ber.* 16, 2239).

Acid residues can also be introduced into the aceto-acetic esters by allowing esters of substituted fatty acids to act upon the sodium compounds. In this way are obtained ketone-dicarboxylic esters. Chlorformic ester produces:—

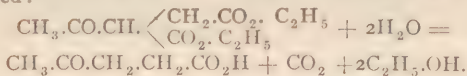
**Aceto-malonic Ester**,  $\text{C}_2\text{H}_3\text{O.CHNa.CO}_2\text{C}_2\text{H}_5 + \text{ClCO}_2\text{C}_2\text{H}_5 = \text{C}_2\text{H}_3\text{O.CH} \begin{matrix} \text{CO}_2\text{C}_2\text{H}_5 \\ \text{CO}_2\text{C}_2\text{H}_5 \end{matrix} + \text{NaCl}$ . This is a mobile liquid which boils at  $240^\circ$  (*Ann.*, 214, 35).

By the action of ethyl chloracetic ester,  $\text{CH}_2\text{Cl.CO}_2\text{C}_2\text{H}_5$ , upon sodaceto-acetic ester:—

**Aceto-succinic Ester**,  $\text{CH}_3\text{CO.CH} \begin{matrix} \text{CH}_2\text{CO}_2\text{C}_2\text{H}_5 \\ \text{CO}_2\text{C}_2\text{H}_5 \end{matrix} = \text{C}_{10}\text{H}_{16}\text{O}_5$ , is formed. It boils at  $254\text{--}256^\circ$ . Concentrated aqueous or alcoholic potash decomposes it almost completely into acetic and succinic acids:—



Baryta water or acids, on the other hand, will induce the ketone-decomposition (p. 218); carbon dioxide is split off and  $\beta$ -aceto-propionic acid (p. 224), a  $\gamma$ -ketonic acid, is produced:—



The two decomposition reactions occur simultaneously in the case of esters of aceto-succinic acid (true also of esters of higher aceto-dicarboxylic acids), just as with the acet-mono-carboxylic acids (p. 218).

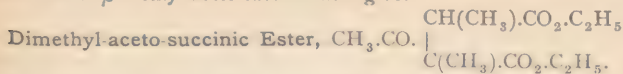
By methylating aceto succinic ester or by letting chloracetic ester act upon methyl aceto-acetic ester (its Na compound), we obtain  $\alpha$ -**Methyl aceto-succinic Ester**,  $\text{CH}_3\text{CO} \begin{matrix} \text{CH}_2\text{CO}_2\text{C}_2\text{H}_5 \\ | \\ \text{C}(\text{CH}_3)\text{CO}_2\text{C}_2\text{H}_5 \end{matrix} = \text{C}_{11}\text{H}_{18}\text{O}_5$ . This boils at  $263^\circ$ . By the acid-decomposition it affords methylsuccinic acid (ordinary pyrotartaric acid), by the ketone-decomposition (separation of  $\text{CO}_2$ )  $\beta$ -aceto-butyric acid (p. 225):—



**Isomeric  $\beta$ -Methyl-aceto-succinic Ester**,  $\begin{matrix} \text{CH}(\text{CH}_3)\text{CO}_2\text{C}_2\text{H}_5 \\ | \\ \text{CH}_3\text{CO.CH.CO}_2\text{C}_2\text{H}_5 \end{matrix} = \text{C}_{11}\text{H}_{18}\text{O}_5$

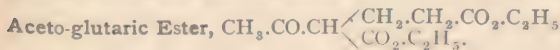
is obtained by the action of  $\alpha$ -bromopropionic ester,  $\text{CH}_3\text{CHBr.CO}_2\text{C}_2\text{H}_5$ , upon aceto-acetic ester. Boils at  $262\text{--}263^\circ$ . Methylsuccinic acid is the re-

sult of its acid-decomposition and  $\beta$ -aceto-isobutyric acid,  $\text{CH}_3\text{CO}\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$ , (p. 225) of the ketone-decomposition. The introduction of methyl into the esters of  $\beta$ -methyl-aceto-succinic acid gives



The acid-decomposition affords symmetrical dimethyl-succinic acid.

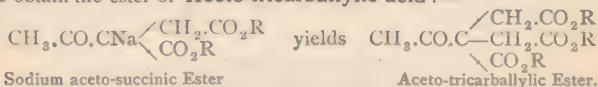
$\beta$ -Iodopropionic ester converts sodium aceto-acetic ester into the



By the elimination of acetyl from this we get glutaric acid, *i. e.*, normal pyrotartaric acid,  $\text{CH}_2(\text{CH}_2\text{CO}_2\text{H})_2$ .

Many other dibasic ketonic acids may be prepared in an analogous manner (*Annalen* 216, 39 and 127).

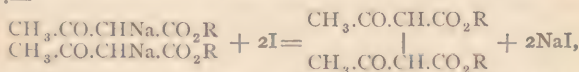
Should sodaceto-succinic ester act a second time upon the ester of chloracetic acid we obtain the ester of **Aceto-tricarballic acid** :—



By the acid-decomposition we get from this acetic and tricarballic acid,

$\text{CH}(\text{CH}_2\text{CO}_2\text{H})_3$  Other ketone-tricarboxylic and tricarboxylic acids may be produced in an analogous manner.

Iodine acting upon sodaceto-acetic ester affords **Diaceto-succinic Ester**,  $\text{C}_{12}\text{H}_{18}\text{O}_6$  :—



a crystalline compound, fusing at  $78^\circ$ . Boiling dilute sulphuric acid converts it into *carbopyrotritartaric acid*,  $\text{C}_8\text{H}_8\text{O}_5$ , a monobasic acid, melting at  $230^\circ$ , and decomposing into  $\text{CO}_2$  and pyrotritartaric, or *uvinic acid*,  $\text{C}_7\text{H}_8\text{O}_3$ . The latter also appears in the distillation of tartaric acid (along with pyroracemic acid), and on heating racemic acid with baryta. It crystallizes in needles, which melt at  $135^\circ$  and fused with caustic soda, yield benzoic acid. Both acids are probably unsaturated ketone-carboxylic acids (*Berichte* 17, 64, 317).

The above methods will also afford from the ester of propionic acid— $\text{CH}_3\text{CH}_2\text{CO}_2\text{R}$ —**Propio-piopic Ester**,  $\text{CH}_3\text{CH}_2\text{CO}\cdot\text{CH}_2\text{CH}_2\text{CO}_2\text{R}$ —the ester of a  $\gamma$ -ketonic acid (p. 225).

Sodium or sodium ethylate acting on ethyl succinic ester yields the so-called **Succino-succinic Ester**,  $\text{C}_{12}\text{H}_{16}\text{O}_6$  (*Annalen* 211, 306, *Berichte* 16, 1411):



Ammonia, sodium, or sodium ethylate (*Ber.*, 16, 133, 1554) produces the same from the ester of bromaceto-acetic acid. It crystallizes in large, triclinic prisms, melting at 126–127°. It is insoluble in water, but readily dissolves in alcohol, ether, etc., forming a bright blue, fluorescent liquid. Ferric chloride imparts a cherry-red color to its alcoholic solution. Two hydrogen atoms in it (of the CH groups) can be replaced by metals. When it is saponified away from air contact by dilute alkalis free **succino-succinic acid**,  $C_6H_6O_2(CO_2H)_2$ , is formed and by the splitting-off of  $CO_2$ , the so-called **succino-propionic acid**,  $C_6H_7O_2CO_2H$ , and the **diketone**,  $C_6H_8O_2$  (isomeric with quinone tetrahydride). If bromine should act on succino-succinic ester 2 hydrogen atoms are withdrawn from the latter and **hydroquinone-dicarboxylic ester**,  $C_{12}H_{14}O_6 = C_6H_4O_2(CO_2.C_2H_5)_2$ , results. This is also prepared by treating dibromaceto-acetic ester with sodium or sodium ethylate (*Ann.*, 219, 78). It fuses at 130°, and when saponified yields free **hydroquinone dicarboxylic acid**,  $C_6H_4O_2(CO_2H)_2$ . On distillation this affords hydroquinone,  $C_6H_6O_2$ , with bromine bromanil,  $C_6Br_4O_2$ , and with nitric acid, nitranilic acid. All these compounds contain a closed chain of six carbon atoms, consequently are closely allied to benzene, and therefore readily afford true benzene derivatives (hydroquinone, bromanil). When chloroform acts upon sodaceto-acetic ester, oxyvitic acid, another benzene compound, is produced.

### 3. $\gamma$ -Ketonic Acids.

These have the ketone oxygen atom attached to the third carbon atom from the carboxyl group (p. 214) and are distinguished from the acids of the  $\beta$ -variety by the fact that they are stable in a free condition even when heated. By the addition of two hydrogen atoms they yield  $\gamma$ -oxy-acids, which immediately pass into lactones (see these).

**$\beta$ -Aceto-propionic Acid**,  $CH_3.CO.CH_2.CH_2.CO_2H = C_5H_8O_5$ , **Lævulinic Acid**. This is isomeric with methyl aceto-acetic acid which may be designated  $\alpha$ -aceto-propionic acid (p. 214). It is obtained from aceto-succinic ester (p. 222) on boiling with hydrochloric acid or baryta water, and from cane sugar, lævulose, inulin, cellulose and gum arabic, on treating them with dilute hydrochloric or sulphuric acid. Stronger action will also convert dextrose and milk sugar into lævulinic acid (*Ann.*, 206, 226).

*Preparation.*—Heat 1 kilo sugar, 1 kilo water and 100 grams  $H_2SO_4$ , for several days, upon a water bath, as long as brown humus substances separate, then press out the pasty mass, wash with water and extract with ether. The lævulinic acid remaining after the evaporation of the ether is purified by distillation (*Ann.*, 206, 207 and 210; 208, 105).

Lævulinic acid dissolves very readily in water, alcohol and ether, and crystallizes in scales, melting at 33.5°. The acid boils with slight decomposition at 239°. Traces of moisture lower the melting point. The molecular refractions of the free acid and its esters confirm the idea of its being a ketonic acid (p. 40). In accordance with this view it yields  $\gamma$ -isonitrosovaleric acid (p. 183) with hydroxylamine.

The *calcium salt*,  $(C_5H_7O_3)_2Ca + 2H_2O$ , forms delicate needles; the *barium salt* is a gummy mass. The *methyl ester*,  $C_5H_7(CH_3)O_3$ , boils at  $191^\circ$ , the *ethyl ester* at  $200^\circ$ .

When heated to  $150-200^\circ$  with hydriodic acid and phosphorus, lævulinic acid is changed to normal valeric acid. By the action of sodium amalgam sodium  $\gamma$ -oxyvalerate is produced. The acid liberated from this becomes valerolactone. Dilute nitric acid converts lævulinic acid (analogous to the oxidation of ketones, p. 162) into acetic and malonic acid and again into succinic acid and  $CO_2$ .

**$\beta$ -Aceto-butyrlic Acid**,  $CH_3.CO.CH \begin{smallmatrix} < CH_3 \\ CH_2.CO_2H \end{smallmatrix} = C_6H_{10}O_3$ , is obtained from  $\alpha$ -methyl aceto-succinic ester (p. 222). It boils at  $242^\circ$  and becomes crystalline at  $-12^\circ$ . The ethyl ester boils near  $205^\circ$ . The isomeric

**$\beta$ -Aceto-isobutyric Acid**,  $CH_3.CO.CH \begin{smallmatrix} CH_3 \\ > CH.CO_2H \end{smallmatrix} = C_6H_{10}O_3$ , from  $\beta$ -methyl aceto-succinic ester, boils at  $248^\circ$ . Its ethyl ester boils at  $207^\circ$ .

Nitric acid oxidizes both acids to  $CO_2$  and methyl succinic acid (pyrotartaric acid).

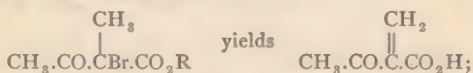
**$\beta$ -Propio-propionic Acid**,  $CH_3.CH_2.CO.CH_2.CH_2.CO_2H = C_6H_{10}O_3$ , is as yet only known in its ester. The latter is obtained by acting with sodium upon the ester of propionic acid (p. 223). It is an agreeably smelling liquid, boiling at  $198-200^\circ$ , and is not colored by ferric chloride.

#### $\delta$ -Ketonic Acid.

**$\gamma$ -Aceto-butyrlic Acid**,  $CH_3.CO.CH_2.CH_2.CH_2.CO_2H = C_6H_{10}O_3$ , is obtained from the ester of aceto-glutaric acid (p. 223) by the withdrawal of  $CO_2$ . It melts at  $13^\circ$  and boils at  $275^\circ$ . Sodium amalgam converts it into a salt of  $\delta$ -oxycaproic acid, which yields a  $\delta$ -lactone (*Ann.*, 216, 127).

## UNSATURATED KETONIC ACIDS.

These are obtained from the brom-alkyl-aceto-acetic esters by the action of alcoholic potash, or when heated alone with water:—



therefore they may be termed aceto-acrylic acids (*Berichte*, 16, 486, 1870).

**Aceto-acrylic Acid**,  $C_5H_6O_3 = C_2H_3O.C \begin{smallmatrix} \diagup CH_2 \\ \diagdown CO_2H \end{smallmatrix}$  (Tetrinic acid), is soluble in alcohol, ether and hot water. It crystallizes in long needles or prisms, melting at  $189^\circ$  and boiling at  $262^\circ$ . Ferric chloride gives it a violet color. With bromine it yields an addition product.

**$\alpha$ -Aceto-crotonic Acid**,  $C_6H_8O_3 = C_2H_3O.C \begin{smallmatrix} \diagup CH.CH_3 \\ \diagdown CO_2H \end{smallmatrix}$  (Pentinic acid), is obtained by heating brom-ethyl aceto-acetic ester to  $100^\circ$  (with separation of  $C_2H_5Br$ ). It melts at  $126.5^\circ$ , sublimes in needles, and is colored a cherry-red by ferric chloride.

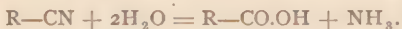


## CYANOGEN COMPOUNDS.

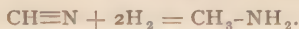
The monovalent group CN, in which trivalent nitrogen is linked with three affinities to carbon  $N \equiv C-$ , is capable of forming quite a number of different derivatives. It shows in many respects great similarity to the halogens, chlorine, bromine, and iodine. Like these, it combines with hydrogen, forming an acid, and combines with the metals to salts which resemble and are frequently isomorphous with the haloid salts. Thus, the alkali salts assume the cube form in crystallizing, and silver cyanide is in all respects like silver chloride. Potassium and sodium burn in cyanogen gas, as in chlorine, forming cyanides. The monovalent group CN cannot exist free, but it doubles itself, just as all other monovalent groups, *e.g.*,  $CH_3$ , when it separates from its compounds and we get the molecule:—

**Dicyanogen**,  $C_2N_2 = NC-CN$ .

In organic cyanogen compounds where CN is attached to alkyls the union of the cyanogen group is very firm. Yet the nitrogen atom in CN can be easily liberated as ammonia, and the carbon atom will pass into the carboxyl group,  $CO_2H$ . *This behavior is characteristic of cyanogen derivatives.* It may be effected by the absorption of water, which can occur by boiling with acids and alkalis:—

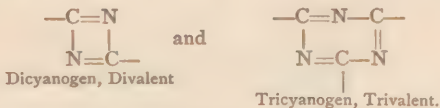


Nascent hydrogen causes a partial separation of nitrogen, producing amines:—



An oxygen atom can be inserted into the CH group—see cyanic acid.

A similar, partial separation accounts also for the condensation of the cyan-group to polymeric forms, *e.g.*, **dicyanogen**,  $C_2N_2$ , and **tricyanogen**,  $C_3N_3$ . The following formulas express their structure:—

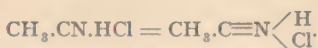


Very many cyanogen derivatives readily adapt themselves to such polymerizations.

Besides the above normal cyanogen derivatives there also exist isomeric *Pseudo-* and *Iso-*cyanogen compounds. These will receive attention further on (with the cyanic acids and carbylamines).

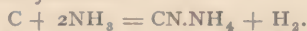
The nitrogen atom in the cyanogen group is trivalent; it may be considered as ammonia in which carbon replaces the hydrogen atoms. This would explain why so many cyanogen derivatives, just as the amides, combine directly with the haloid acids and

metallic chlorides, yielding compounds similar to the ammonium salts:—



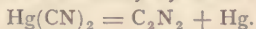
These are, however, unstable. Perhaps it is necessary to admit (p. 209) that the halogen hydride has effected an entrance for itself in the CN group (as in  $\text{CH}_3.\text{CCl} = \text{N}.\text{CH}_3$ ).

Yellow prussiate of potash and potassium cyanide serve as starting-out substances in the preparation of the cyanogen derivatives. Potassium cyanide is obtained by the ignition of nitrogenous organic matter with KOH or potashes (see Text-Book of Inorganic Chemistry). The direct union of carbon and nitrogen to cyanogen is only effected with difficulty. It may be accomplished by conducting nitrogen over a mixture of carbon and metallic potassium or potassium carbonate raised to a red heat. Potassium cyanide is then formed. The yield is more abundant if ammonia gas be conducted over the mixture. The ignition of carbon in ammonia gas furnishes ammonium cyanide:—



All these methods, however, are not applicable on a large scale.

**Free Cyanogen** or **Dicyanogen**,  $\text{C}_2\text{N}_2 = \text{NC}.\text{CN}$ , is present in small quantity in the gases of the blast furnace. It is obtained by the ignition of silver or mercury cyanide:—

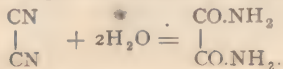


Its preparation from ammonium oxalate through the agency of heat is of theoretical interest:—



It is on this account to be considered as the nitrile of oxalic acid.

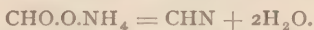
Cyanogen is a colorless, peculiar-smelling, poisonous gas, of specific gravity 26 ( $\text{H} = 1$ ). It may be condensed to a mobile liquid by cold of  $-25^\circ$ , or by a pressure of four atmospheres at ordinary temperatures. In this condition it has a sp. gr. 0.866, solidifies at  $-34^\circ$  to a crystalline mass, and boils at  $-21^\circ$ . It burns with a bluish-purple mantled flame. Water dissolves 4 volumes and alcohol 23 volumes of the gas. On standing the solutions become dark and break up into ammonium oxalate and formate, hydrogen cyanide and urea, and at the same time there separates a brown body—the so-called *azulmic acid*,  $\text{C}_4\text{H}_5\text{N}_5\text{O}$ . With aqueous potash cyanogen yields potassium cyanide and isocyanate. In these reactions the molecule splits, and if a slight quantity of aldehyde be present in the aqueous solution only oxamide results:—



With hydrogen sulphide cyanogen yields *hydroflavic acid*,  $C_2N_2 \cdot H_2S = \begin{array}{c} CN \\ | \\ CS.NH_2 \end{array}$  and *hydrorubianic acid*,  $C_2N_2 \cdot 2H_2S = \begin{array}{c} CS.NH_2 \\ | \\ CS.NH_2 \end{array}$  The first consists of yellow crystals, the second of red.

On heating mercuric cyanide there remains a dark substance, *paracyanogen*, a polymeric modification,  $(C_2N_2)_n$ . Strong ignition converts it again into cyanogen. It yields potassium cyanate with caustic potash.

**Hydrocyanic Acid, CNH, Prussic Acid**, is obtained from various plants containing amygdalin (from cherry-stones, bitter almonds, etc.), on standing in contact with water, when the amygdalin undergoes a fermentation, breaking up into hydrocyanic acid, sugar and oil of bitter almonds. Its production from ammonium formate by the application of heat is of theoretic interest:—



This reaction would show it to be the nitrile of formic acid.

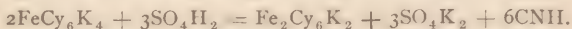
Hydrogen cyanide may also be obtained by passing the silent electric discharge through a mixture of  $C_2N_2$  and hydrogen:—



The metallic cyanides yield it when they are distilled with mineral acids.

Anhydrous hydrocyanic acid is a mobile liquid, of specific gravity 0.697 at  $18^\circ$ , and becomes a crystalline solid at  $-15^\circ$ . It boils at  $+26.5^\circ$ . Its odor is peculiar and resembles that of oil of bitter almonds. The acid is extremely poisonous.

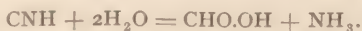
The following procedure serves for the preparation of aqueous prussic acid. Finely pulverized yellow prussiate of potash (10 parts) is covered with a cooled mixture of sulphuric acid (7 parts) and water (10 to 40 parts, according to the desired strength of the prussic acid), and then distilled from a retort provided with a condenser. The heat of a sand-bath is necessary. The decomposition of the yellow prussiate occurs according to the equation:—



About half the cyanogen contained in the ferrocyanide is converted into hydrocyanic acid.

The anhydrous acid can be obtained from the hydrous by fractional distillation and dehydration by calcium chloride.

The aqueous acid decomposes readily upon standing, yielding ammonium formate and brown substances. The presence of a very slight quantity of stronger acid renders it more stable. When warmed with alkalis or mineral acids it breaks up into formic acid and ammonia:—



Nascent hydrogen (zinc and hydrochloric acid) reduces it to methylamine (p. 226).

Hydrocyanic acid is a feeble acid, and imparts a faint red to

blue litmus. Like the haloid acids, it reacts with metallic oxides, producing metallic cyanides. From solutions of silver nitrate it precipitates silver cyanide, a white, curdy precipitate:\*

To detect small quantities of free prussic acid or its soluble salts, saturate the solution under examination with caustic potash, add a solution of a ferrous salt, containing some ferric salt, and boil for a short time. Add hydrochloric acid to dissolve the precipitated iron oxides. If any insoluble Prussian blue should remain, it would indicate the presence of hydrocyanic acid. The following reaction is more sensitive. A few drops of yellow ammonium sulphide are added to the prussic acid solution, and this then evaporated to dryness. Ammonium sulphocyanide will remain, and if added to a ferric salt, will color it a deep red.

Dry prussic acid combines directly with the gaseous halogen hydrides (p. 227), affording crystalline compounds like  $\text{CHN.HCl}$ , easily soluble in water and ether. The aqueous solutions rapidly decompose, yielding formic acid and ammonium salts. The acid also unites with some metallic chlorides, *e. g.*,  $\text{Fe}_2\text{Cl}_6$ ,  $\text{SbCl}_5$ .

#### HALOGEN COMPOUNDS OF CYANOGEN.

These result by the action of the halogens upon metallic cyanides. The chloride and bromide can condense to tricyanides, in which we assume the presence of the tricyanogen group,  $\text{C}_3\text{N}_3$  (p. 226).

**Cyanogen Chloride**,  $\text{CNCl}$ , is produced by acting with chlorine upon aqueous hydrocyanic acid. It is a mobile liquid, solidifying at  $-5^\circ$ , and boiling at  $+15.5^\circ$ . It is heavier than water, and only slightly soluble in it, but readily dissolved by alcohol and ether. Its vapors have a penetrating odor, provoking tears, and acting as a powerful poison.

In preparing it, saturate a cold mercuric cyanide solution with chlorine. The cyanogen chloride which escapes on the application of heat, is conducted through a tube filled with copper turnings, to free it of chlorine. Or strongly cooled prussic acid (containing 20 per cent.  $\text{CNH}$ ), is saturated with chlorine gas, the oily cyanogen chloride separated, and then distilled over mercuric oxide, to remove excess of prussic acid.

\* In hydrocyanic acid the hydrogen, replaceable by metals, is in union with carbon, whereas, ordinarily, it is only the hydrogen of hydroxyl (in acids and alcohols) that possesses the power of this kind of replacement. The acetylenes, nitro-paraffins (p. 79), aceto acetic esters (p. 216) and the analogously constituted malonic esters manifest a similar deportment. In these compounds, two or three carbon valences are generally saturated by negative elements or groups, and they manifest also analogous behavior, in that their alkali salts are less stable than those with the heavy metals.

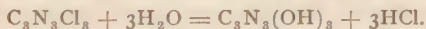
The hydrogen attached to nitrogen possesses also the function of acid hydrogen, if two affinities of the nitrogen are combined with negative groups, as in the imides:—



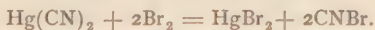


Cyanogen chloride combines with different metallic chlorides. With ammonia, it affords ammonium chloride and cyanamide,  $\text{CN.NH}_2$ . Alkalies decompose it into metallic cyanides and isocyanates.

**Tricyanogen Chloride**,  $\text{C}_3\text{N}_3\text{Cl}_3$ , *solid chlorcyan*, is produced when the liquid chlorine is kept in sealed tubes. It is formed directly by leading chlorine into an ethereal solution of  $\text{CNH}$ , or into anhydrous hydrocyanic acid exposed to direct sunlight. It appears, too, in the distillation of cyanuric acid,  $\text{C}_3\text{O}_3\text{N}_3\text{H}_3$ , with phosphorus pentachloride. It crystallizes in shining needles or leaflets, melts at  $145^\circ$ , and boils at  $190^\circ$ . It is not very soluble in cold water, but readily in alcohol and ether. Its vapor density equals 92 ( $\text{H} = 1$ ). When boiled with acids or alkalies, it breaks up into hydrochloric and cyanuric acids:—



**Cyanogen Bromide**,  $\text{CNBr}$ , is obtained when bromine acts on anhydrous prussic acid or upon mercuric cyanide:—



It is a very volatile, crystalline substance, readily soluble in water, alcohol and ether. On heating the anhydrous bromide or its ethereal solution in sealed tubes to  $130$ – $140^\circ$ , it becomes polymeric **tricyanogen bromide**,  $\text{C}_3\text{N}_3\text{Br}_3$ . The latter is more easily obtained by heating dry yellow or red prussiate of potash with bromine to  $250^\circ$  (*Ber.*, 16, 2893). It is an amorphous white powder, soluble in ether and benzene. It melts above  $300^\circ$ , and is volatile at higher temperatures. It decomposes in moist air, or upon boiling with water, into  $\text{HBr}$  and cyanuric acid.

**Cyanogen Iodide**,  $\text{CNI}$ , is prepared by subliming a mixture of mercuric cyanide (1 molecule) and iodine (2 molecules); or by adding iodine to a concentrated aqueous solution of potassium cyanide. The cyanogen iodide which results is withdrawn by ether. It has a sharp odor, dissolves in water, alcohol and ether, and sublims without melting, near  $45^\circ$ , in brilliant white needles. Ammonia converts it into cyanamide and ammonium iodide.

## METALLIC DERIVATIVES OF CYANOGEN.

The metallic derivatives of cyanogen have already been considered in inorganic chemistry. Here attention will only be directed to certain generalizations.

The properties of and the methods of preparing the metallic cyanides vary greatly. The alkali cyanides may be formed by the direct action of these metals upon cyanogen gas; thus, potassium burns with a red flame in cyanogen, at the same time yielding potassium cyanide,  $\text{C}_2\text{N}_2 + \text{K}_2 = 2\text{CNK}$ . The strongly basic metals dissolve in hydrocyanic acid, separating hydrogen and forming cyanides. A more common procedure is to act with the acid upon metallic oxides and hydroxides:—

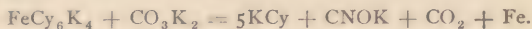


The insoluble cyanides of the heavy metals are obtained by the double decomposition of the metallic salts with potassium cyanide.

The cyanides of the light metals, especially the alkali and alkaline earths are easily soluble in water, react alkaline and are decomposed by acids, even carbon dioxide, with elimination of hydrogen cyanide; yet they are very stable, even at a red heat, and sustain no change. The cyanides of the heavy metals, however, are mostly insoluble, and are only decomposed, or not at all, by the strong acids. When ignited the cyanides of the noble metals suffer decomposition, breaking up into cyanogen gas and metals.

The following simple cyanides may be mentioned:—

*Potassium Cyanide*, KCN, crystallizes in cubes or octahedra and fuses at a bright red heat to a clear liquid. In moist air it deliquesces and gives up (by the action of carbon dioxide) hydrogen cyanide. It is scarcely soluble in absolute alcohol, but dissolves readily in aqueous alcohol. The best mode of preparing chemically pure potassium cyanide consists in conducting prussic acid into an alcoholic solution of KOH (in 90 per cent. alcohol). Take 1 part KOH for 3 parts of the yellow prussiate (p. 228). The potassium cyanide separates as a powder or jelly, which is drained upon a filter. The so called Liebig potassium cyanide, occurring in trade, contains potassium cyanide and isocyanate. It is made by igniting a mixture of dry yellow prussiate of potash (8 parts) with pure potashes (3 parts):—



At present chemically pure potassium cyanide is obtained by mere ignition of potassium ferrocyanide:—



The exceedingly finely divided iron carbide which adheres to the salt is removed by filtering the molten mass through porous clay crucibles.

The aqueous or alcoholic solution becomes brown on exposure, and when boiled, rapidly decomposes into potassium formate and ammonia. If fused in the air or with metallic oxides which are readily reduced, potassium cyanide absorbs oxygen, and is converted into potassium isocyanate. When fused with sulphur it yields potassium thiocyanate.

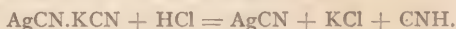
*Ammonium Cyanide*,  $\text{NH}_4\text{CN}$ , is formed by the direct union of CNH with ammonia, by heating carbon in ammonia gas, and by conducting carbon monoxide and ammonia through red-hot tubes. It is best prepared by subliming a mixture of potassium cyanide or dry ferrocyanide with ammonium chloride. An aqueous solution of it may be made by distilling the solution of ferrocyanide and ammonium chloride. It affords colorless cubes, easily soluble in alcohol and subliming at  $40^\circ$ , with partial decomposition into  $\text{NH}_3$  and CNH. When preserved it becomes dark in color and decomposes.

*Mercuric Cyanide*,  $\text{Hg}_2(\text{CN})_2$ , is obtained by dissolving mercuric oxide in hydrocyanic acid, or by boiling Prussian blue (8 parts) and mercuric oxide (1 part) with water, until the blue coloration disappears. It dissolves readily in hot water (in 8 parts cold water), and crystallizes in bright, shining, quadratic prisms. When heated it yields cyanogen and mercury (p. 227).

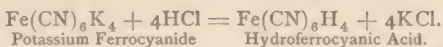
*Silver Cyanide*,  $\text{AgCN}$ , is precipitated as a white, curdy compound from silver solutions by potassium cyanide or prussic acid. It resembles silver chloride very much. It darkens on exposure to the air, and dissolves readily in ammonium hydrate and potassium cyanide.

From some reactions, it would seem that silver cyanide may contain the isocyanogen group,  $\text{C} \equiv \text{N} -$ , and that silver, consequently, is linked to nitrogen (as in silver nitrite,  $\text{NO}_2\text{Ag}$ , p. 78). Compare Carbylamines (p. 246).

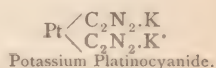
**Compound Metallic Cyanides.** The cyanides of the heavy metals insoluble in water dissolve in aqueous potassium cyanide, forming crystallizable double cyanides, which are soluble in water. Most of these compounds behave like double salts. Acids decompose them in the cold, with disengagement of hydrocyanic acid and the precipitation of the insoluble cyanides:—



In others, however, the metal is in more intimate union with the cyanogen group, and the metals in these cannot be detected by the usual reagents. Iron, cobalt, platinum, also chromium and manganese in their *ic* state, form cyanogen derivatives of this class. The stronger acids do not eliminate prussic acid from them, even in the cold, but hydrogen acids are set free, and these are capable of producing salts:—



It may be assumed that polymeric cyanogen groups—dicyanogen and tricyanogen (p. 226)—are present in these derivatives of cyanogen:—



This view is sustained by the fact that these cyanides, although soluble in water, are yet not poisonous. We do not know of a sharp line of difference between cyanides of the first and those of the second variety; different compounds, *e. g.*, potassium gold cyanide,  $\text{Au(CN)}_4\text{K}$ , show an intermediate behavior. The most important compound cyanides have been already treated in the Inorganic Chemistry.

**Nitroprussides.** These arise on treating the ferrocyanides with nitric acid. The most important of them is

**Sodium Nitroprusside.** Its constitution has not yet been definitely determined (*Ber.*, 15, 2613). The simplest expression of it is given by the formula,  $\text{Fe(CN)}_5(\text{NO})\text{Na}_2 + 2\text{H}_2\text{O}$ . It crystallizes in beautiful red rhombic prisms, readily soluble in water. Sunlight decomposes it into nitrogen oxide and Prussian blue.

**Preparation.**—Heat pulverized potassium ferrocyanide with two parts concentrated nitric acid, diluted with an equal volume of water, until ferric chloride ceases to produce a blue precipitate. The cooled solution is filtered off from the separated saltpetre, saturated with soda, and evaporated until near the point of crystallization, when 3–4 parts of alcohol are added.

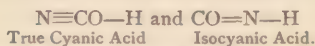
Sodium nitroprusside serves as a very delicate reagent for alkali-

line sulphides, which give with it an intense violet coloration even in very dilute solution.

It yields precipitates with most of the heavy metals. When hydrochloric acid is added to the nitroprussides, *hydrogen nitroprusside*,  $\text{Fe}(\text{CN})_5(\text{NO})\text{H}_2 + \text{H}_2\text{O}$ , is liberated. This crystallizes in vacuo from its aqueous solution, in dark-red prisms.

## OXYGEN COMPOUNDS OF CYANOGEN.

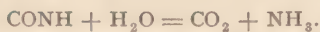
The empirical formula,  $\text{CNOH}$ , of cyanic acid, has two possible structures:—



The known, ordinary cyanic acid and its salts probably correspond to the second formula, hence it is designated *isocyanic acid* or *carbimide*,  $\text{CO}:\text{NH}$  (imide of carbonic acid). It is certain the esters of ordinary cyanic acid are constituted according to the second formula, and must be considered as isocyanic esters. True cyanic acid,  $\text{CN.OH}$ , and its salts are not known, but esters of it, *e. g.*,  $\text{CN.O.CH}_3$ , do exist, and these are also designated *cyanetholins* (p. 235).

Ordinary **Cyanic Acid**,  $\text{CONH}$ , isocyanic acid or carbimide. It is obtained by heating polymeric cyanuric acid. The vapors which distil over are condensed in a strongly cooled receiver.

The acid is only stable below  $0^\circ$ , and is a mobile, very volatile liquid, which reacts strongly acid, and smells very much like glacial acetic acid. It produces blisters upon the skin. Above  $0^\circ$ , the aqueous solution is rapidly converted into carbon dioxide and ammonia:—



At  $0^\circ$ , the aqueous cyanic acid passes rapidly into the polymeric *cyamelid*—a white, porcelain-like mass, which is insoluble in water, and when distilled reverts to cyanic acid. Above  $0^\circ$ , the conversion of liquid cyanic acid into cyamelide occurs, accompanied by explosive foaming. Cyanic acid dissolves in alcohols, yielding esters of allophanic acid.

The salts of the above acid are obtained by double decomposition from the potassium salt; those of the heavy metals are insoluble in water, and those of the earths are precipitated by alcohol. Heat decomposes both varieties into  $\text{CO}_2$  and salts of cyanamide (see this).

**Potassium Isocyanate**,  $\text{CO}:\text{NK}$ , *ordinary cyanate of potassium*, is formed in the oxidation of potassium cyanide in the air or with readily reducible metallic oxides ( $\text{CNK} + \text{O} = \text{CO}:\text{NK}$ ). It results, too, on conducting dicyanogen, or cyanogen chloride into caustic potash (*Ber.*, 13, 2201). The salt crystallizes in shining leaflets, resembling potassium chlorate, and dissolves readily in cold

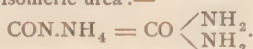


water, but with more difficulty in hot alcohol. In aqueous solution it decomposes rapidly into ammonia and potassium carbonate.

*Preparation.*—Fuse in a crucible a mixture of dehydrated yellow prussiate of potash (8 parts), potashes (3 parts), and gradually add, while stirring, lead oxide or minium (15 parts):  $\text{CNK} + \text{PbO} = \text{CNOK} + \text{Pb}$ . The reduced lead melts together on the bottom of the vessel. The white mass is poured out and the potassium cyanate extracted with alcohol.

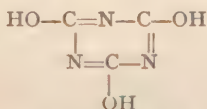
Potassium isocyanate precipitates aqueous solutions of the heavy metals. The lead, silver and mercurous salts are white, the cupric salt is green in color.

*Ammonium cyanate*,  $\text{CN.O.NH}_4$  or  $\text{CO:N(NH}_4\text{)}$ , is a white crystalline powder, formed by contact of cyanic acid vapors with dry ammonia. Caustic potash decomposes it into potassium isocyanate and ammonia. On evaporating the aqueous solution it passes into isomeric urea:—



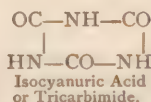
The cyanates of the primary and secondary amines are similarly converted into alkylic ureas, whereas the salts of the tertiary amines remain unchanged.

Three molecules of  $\text{CNOH}$  condense to *Tricyanic* or *Cyanuric Acid*,  $\text{C}_3\text{N}_3\text{O}_3\text{H}_3$  (p. 226). Here again two structural cases are possible:—



True Cyanuric Acid

and



The second formula in all probability represents ordinary cyanuric acid, and in consequence is termed *isocyanuric acid* or *tricarbimide*. The esters of isocyanuric acid result when the isocyanurates are treated with alkyl iodides. Their structure corresponds to the second formula. Real cyanuric acid and its salts are unknown. Esters exist, and these are isomeric with the isocyanuric esters.

It was formerly believed that the first formula represented the structure of ordinary isocyanuric acid and its salts, because they could be obtained from tricyanogen chloride by the action of water or the alkalis, and conversely tricyanogen chloride was formed by acting on them with phosphoric chloride. In producing the esters from the salts it was supposed that a molecular transposition occurred. The relations of cyanuric acid to tricyanogen chloride are to be interpreted in the same manner as the formation of the imid-chlorides from the amides of the acids, and the conversion of the former into the latter through the agency of water (p. 209). The entire deportment of cyanuric acid and its salts argues for the view that it is tricarbimide. Its production from carbonyldiurea (see this) proves this.

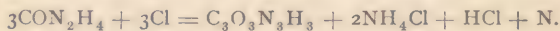
**Ordinary Cyanuric Acid**,  $\text{C}_3\text{O}_3\text{N}_3\text{H}_3$ , *isocyanuric acid*, *fulminuric acid*, is obtained from tricyanogen chloride,  $\text{C}_3\text{N}_3\text{Cl}_3$ , by boiling the latter with water and alkalis (see above).

Dilute acetic acid added to a solution of potassium isocyanate,

gradually separates primary potassium isocyanate,  $C_3N_3O_3H_2K$ , from which mineral acids release cyanuric acid. It appears, too, on heating urea :—



*Preparation.*—Carefully heat urea until the disengagement of ammonia ceases and the mass, which at first fused, has become solid again. The residue is dissolved in potash and the cyanuric acid precipitated with hydrochloric acid. A better plan is to lead dry chlorine gas over fused urea at a temperature of 130–140° :—



Cold water is employed to remove the ammonium chloride from the residue, and the latter recrystallized from hot water.

Cyanuric acid is more easily obtained by heating tribromcyanide with water (*Berichte*, 16, 2893).

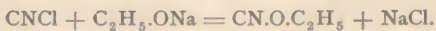
Cyanuric acid crystallizes from aqueous solution with 2 molecules  $H_2O$  ( $C_3N_3O_3H_3 + 2H_2O$ ) in large rhombic prisms. It is soluble in 40 parts cold water, and easily soluble in hot water and alcohol. When boiled with acids it decomposes into carbonic acid and ammonia. When distilled it breaks up into cyanic acid.  $PCl_5$  converts it into tricyanogen chloride.

Cyanuric acid is tribasic and yields three series of salts, all of which crystallize well. The salts of the heavy metals are not soluble in water.

For two isomeric cyanuric acids, see *Berichte*, 12, 170.

## ESTERS OF THE CYANIC ACIDS.

Those of true cyanic acid,  $CN.OH$  (p. 233), result when cyanogen chloride acts upon sodium alcoholates :—

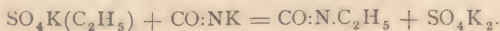


They are also termed *cyanetholins*. They are liquids, of ethereal odor, are insoluble in water, and suffer decomposition when distilled. The ethyl ester is the only one that has been closely studied.

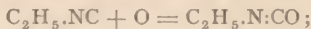
**Ethyl Cyanic Ester**,  $CN.O.C_2H_5$ , *cyanetholin*, is obtained by the action of cyanogen chloride or iodide upon a solution of sodium ethylate in absolute alcohol. On diluting with water it precipitates out in the form of a yellow oil, of sp. gr. 1.127 at 15°. It dissolves readily in alcohol and ether. When boiled with caustic potash it decomposes into  $CO_2$ ,  $NH_3$  and ethyl alcohol. Acid esters of isocyanuric acid are produced when it is boiled with hydrochloric acid. It polymerizes into solid ethyl cyanuric esters after standing some time.

The homologous esters are prepared in a similar manner, but they have been but little investigated.

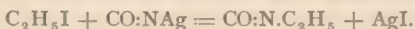
**Esters of Isocyanic Acid**,  $CO:NH$ . *Wurtz* prepared these, in 1848, by distilling potassium ethyl sulphate with potassium isocyanate :—



Esters of isocyanuric acid are formed at the same time, in consequence of polymerization. Isocyanic esters are produced, too, by oxidizing the carbylamines with mercuric oxide:—



and by the action of silver isocyanate upon alkyl iodides:—

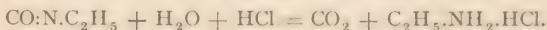


These esters are volatile liquids, boiling without decomposition, and possessing a very disagreeable, penetrating odor, which provokes tears. They are decomposed by water and alcohol, but dissolve without decomposition in ether. On standing they pass rather rapidly into the polymeric isocyanuric esters.

In all their reactions they behave like carbimide derivatives. Heated with KOH they become primary amines and potassium carbonate (p. 124):—

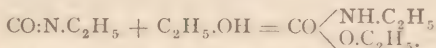


Acids in aqueous solution behave similarly:

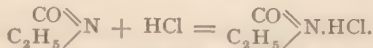


With the amines and ammonia they yield alkylic ureas (see these). Water breaks them up at once into  $\text{CO}_2$  and dialkylic ureas. In this decomposition amines form first,  $\text{CO}_2$  being set free, and these combine with the excess of isocyanic ester to dialkylic ureas (see these).

The esters of isocyanic acid unite with alcohol, yielding esters of carbaminic acid:—



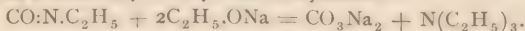
As derivatives of ammonia the isocyanic esters are capable of combining directly with the haloid acids:—



Water decomposes these products at once into  $\text{CO}_2$  and amine salts.

**Methyl Isocyanic Ester**,  $\text{CO}:\text{N}:\text{CH}_3$ , methyl carbimide, is obtained by distilling potassium methyl sulphate with potassium isocyanate. It is a very volatile liquid which boils at  $44^\circ$ . When boiled with KOH it affords methylamine,  $\text{CH}_3\cdot\text{NH}_2$ .

**Ethyl Isocyanic Ester**,  $\text{CO}:\text{N}:\text{C}_2\text{H}_5$ , ethyl carbimide. This boils at  $60^\circ$ , and has the specific gravity of 0.891. It furnishes ethylamine with boiling alkalies; with sodium ethylate it yields triethylamine:—



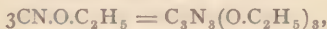
The compound  $\left. \begin{array}{l} \text{CO} \\ \text{C}_2\text{H}_5 \end{array} \right\} \text{N}\cdot\text{HCl}$  (see above) has a penetrating odor, and boils at  $98^\circ$ .

**Isoamyl Isocyanic Ester**,  $\text{CO}:\text{N}:\text{C}_5\text{H}_{11}$ , amyl carbimide, from amyl alcohol of fermentation, boils near  $100^\circ$ .

**Allyl Isocyanic Ester**,  $\text{CO}:\text{N}:\text{C}_3\text{H}_5$ , is obtained by heating allyl iodide and potassium cyanate. It boils at  $82^\circ$ .

## ESTERS OF THE CYANURIC ACIDS.

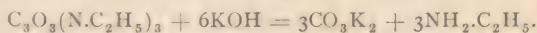
The esters of the *true* cyanuric acid,  $C_3N_3(OH)_3$  (p. 234), form, as already observed, by the polymerization of the cyanic esters (cyanetholines) after long standing :—



and are produced, too, directly, together with the cyanic esters, in the preparation of the latter, by conducting cyanogen chloride into sodium alcoholates. They furnish addition products (*Ber.*, 16, 390) with six atoms of bromine.

**Methyl Cyanuric Ester**,  $C_3N_3(O.CH_3)_3$ , crystallizes in needles, melting at  $132^\circ$ , and is soluble in alcohol and hot water. When digested with potash it breaks up into potassium isocyanate and methyl alcohol. It boils at  $160^\circ$ – $170^\circ$ , but sustains a molecular transposition; the distillate consists of methyl isocyanuric ester. The **ethyl ester**,  $C_3N_3(O.C_2H_5)_3$ , obtained from sodium ethylate and cyanogen bromide, melts at  $29^\circ$ , and at  $250^\circ$  passes into the isocyanic ester.

*Isocyanuric Esters*, (p. 234)—the ordinary cyanuric esters—are produced in the distillation of neutral potassium isocyanurate with potassium ethyl or methyl sulphate. The reaction is similar to that noted in the formation of isocyanic esters (the isocyanuric esters appear in appreciable quantities at the same time with these). We have already spoken of their formation as a result of the molecular transposition of the cyanuric esters. They are solid crystalline bodies, soluble in water, alcohol and ether. They pass into primary amines and potassium carbonate when boiled with alkalis—similar to the isocyanates :—



**Methyl Isocyanuric Ester**,  $C_3O_3(N.CH_3)_3$ , crystallizes in bright prisms. It melts at  $175^\circ$ , and boils undecomposed at  $296^\circ$ . It yields carbonic acid and methylamine when boiled with alkalis.

**Ethyl Isocyanuric Ester**,  $C_3O_3(N.C_2H_5)_3$ , consists of large rhombic prisms, melting at  $95^\circ$  and boiling at  $276^\circ$ . It volatilizes with steam. When boiled with KOH it passes into carbon dioxide and ethylamine. The **diethyl ester**,  $C_3O_3.N_3(C_2H_5)_2H$ , appears in the alcoholic solution of the crude neutral ester obtained by distillation. Sulphuric acid sets it free from the barium salt. It crystallizes in six-sided prisms which melt at  $173^\circ$  and distil undecomposed.

## SULPHUR COMPOUNDS OF CYANOGEN.

The thiocyanic acids are :—

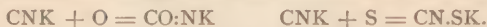


These correspond to the two isomeric cyanic acids (p. 233).

The known thio-cyanic acid and its salts (having the group  $NC.S$  —) are constituted according to the first formula. They are



obtained from the cyanides by the addition of sulphur, just as the isocyanates result by the absorption of oxygen. The different union of sulphur and oxygen in this instance is noteworthy:—



Isothiocabimide,  $\text{CS:NH}$ , and its salts are not known. Its esters (the mustard oils) do, however, exist and are isomeric with those of sulphocyanic acid.

**Thiocyanic Acid**,  $\text{CN.SH}$ , sulphocyanic acid, is obtained by distilling its potassium salt with dilute sulphuric acid, or decomposing the mercury salt with dry  $\text{H}_2\text{S}$  or  $\text{HCl}$ . It is a liquid, with a penetrating odor, and solidifies at  $-12.5^\circ$ . It is soluble in water and alcohol. Its solutions react acid. The free acid and also its salts, color solutions of ferric salts a dark red. The free acid decomposes readily, especially in the presence of strong acids, into hydrogen cyanide and perthiocyanic acid,  $\text{C}_2\text{N}_2\text{S}_3\text{H}_2$ .

The alkali thiocyanates, like the isocyanates, are obtained by fusing the cyanides with sulphur.

*Potassium Thiocyanate*,  $\text{CN.SK}$ , sulphocyanate of potash, crystallizes from alcohol in long, colorless prisms, which deliquesce in the air.

*Preparation*.—Fuse 32 parts sulphur with 17 parts dry potassium carbonate, add 46 parts dehydrated yellow prussiate of potash, and again heat until the latter is completely decomposed. The fusion is finally exhausted with alcohol.

The *sodium salt* is very deliquescent, and occurs in the saliva and urine of different animals.

*Ammonium Thiocyanate*,  $\text{CN.S.NH}_4$ , is formed on heating prussic acid with yellow ammonium sulphide, or a solution of ammonium cyanide with sulphur. It is most readily obtained by heating  $\text{CS}_2$  with alcoholic ammonia:—



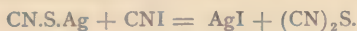
A mixture of 300 parts concentrated ammonia solution, 300 parts strong alcohol, and 70–80 parts carbon disulphide, is permitted to stand for a day. Two-thirds of the liquid are then distilled off (the distillate, consisting of alcohol and some ammonium thiocyanate, may be used in a second preparation), and the residue carefully evaporated until crystallization sets in.

The salt crystallizes in large, clear prisms, which readily dissolve in water and alcohol. It melts at  $147^\circ$ , and at  $170^\circ$  molecular transposition into hiourea occurs (similar to ammonium cyanate (p. 234):—

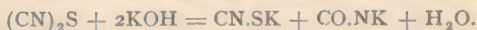


The salts of the heavy metals are mostly insoluble, and are obtained by precipitation. The *mercury salt*,  $(\text{CN.S})_2\text{Hg}$ , is a gray, amorphous precipitate, which, ignited, burns and swells up strongly (Pharaoh's serpents). The *ferric salt*,  $(\text{CN.S})_3\text{Fe}_2$ , is a black, deliquescent mass, which dissolves with a deep red color in water.

**Cyanogen Sulphide**,  $(\text{CN})_2\text{S}$ , is formed when cyanogen iodide in ethereal solution, acts on silver thiocyanate:—



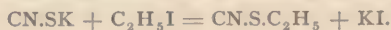
The product is extracted with carbon disulphide, and the solution evaporated. Cyanogen sulphide forms rhombic plates, which melt at  $65^\circ$ , and sublime at  $30^\circ$ . Its odor resembles that of the iodide, and the compound dissolves in water, alcohol and ether. KOH breaks it up into potassium thiocyanate and isocyanate:—



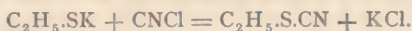
The **trimethyl ester**,  $\text{C}_3\text{N}_3(\text{S.CH}_3)_3$ , of thiocyanuric acid is the only known derivative of this acid. It is produced along with methyl mustard oil on heating methyl sulphocyanate,  $\text{CN.S.CH}_3$  (see below) to  $180^\circ$ . It is a crystalline compound, melting at  $180^\circ$ .

### ESTERS OF THE THIOCYANIC ACIDS.

Those of true thiocyanic acid,  $\text{CN.SH}$ , are obtained by distilling organic salts of sulphuric acid in concentrated aqueous solution with potassium sulphocyanide, or by heating with alkyl iodides:—



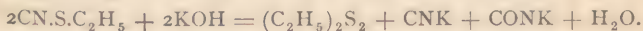
Further, by the action of  $\text{CNCl}$  upon salts of the mercaptans:—



They are liquids, not soluble in water, and possess a leek-like odor. Nascent hydrogen (zinc and sulphuric acid) converts them into hydrocyanic acid and mercaptans:—



With aqueous potash they behave as follows:—



On digesting with alcoholic potash the reaction is:—



The isomeric mustard oils do not afford any potassium sulphocyanate. With  $\text{H}_2\text{S}$  they yield the dithiourethanes, whereas the isomeric mustard oils are not attacked, or decompose into  $\text{CS}_2$  and amines. Boiling nitric acid oxidizes them to alkylsulphonic acids with separation of the cyanogen group.

**Methyl Thiocyanic Ester**,  $\text{CN.S.CH}_3$ , boils at  $133^\circ$ , and has a specific gravity 1.088 at  $0^\circ$ . When heated to  $180$ – $185^\circ$  it is converted into the isomeric methyl-isothiocyanic ester, with simultaneous polymerization to trithiocyanic ester,  $\text{C}_3\text{N}_3\text{S}_3(\text{CH}_3)_3$  (*Ber.*, 13, 1349).

**Ethyl Thiocyanic Ester**,  $\text{CN.S.C}_2\text{H}_5$ , boils at  $142^\circ$ . Its specific gravity equals 1.033 at  $0^\circ$ . It combines directly with the haloid acids.

**Isopropyl Thiocyanic Ester**,  $\text{CN.S.C}_3\text{H}_7$ , boils at  $152$ – $153^\circ$ . The **isoamyl ester**,  $\text{CN.S.C}_5\text{H}_{11}$ , boils at  $197^\circ$ .

**Allyl Thiocyanic Ester**,  $\text{CN.S.C}_3\text{H}_5$ , is formed when allyl iodide or bromide acts upon alcoholic potassium thiocyanate at  $0^\circ$ . When heat is applied allyl

mustard oil,  $\text{CS:N.C}_3\text{H}_5$ , results by molecular transposition. It is produced, too, when  $\text{CNCl}$  acts upon lead allyl mercaptide. A yellow, oily liquid, smelling somewhat like  $\text{CNH}$  and boiling at  $161^\circ$ . Its specific gravity equals 1.071 at  $0^\circ$ . On boiling it rapidly changes to isomeric allyl mustard oil,  $\text{CS:N.C}_3\text{H}_5$ ; at ordinary temperatures the conversion is gradual. In the cold zinc and hydrochloric acid decompose the ester into  $\text{CNH}$  and allyl mercaptan,  $\text{C}_3\text{H}_5\cdot\text{SH}$ .

The esters of isothiocyanic acid,  $\text{CS:NH}$ , are termed mustard oils, from their most important representative. They may also be considered as thiocarbimide derivatives. They are formed:—

1. By mixing carbon disulphide with primary (or secondary) amines in alcoholic, or better, ethereal solution. By evaporation we get amine salts of alkyl carbaminic acids (see these):—



On adding silver nitrate, mercuric chloride or ferric chloride, to the aqueous solution of these salts, formed with primary amines, and then heating to boiling, the metallic compounds first precipitated decompose into metallic sulphides, hydrogen sulphide and mustard oils which distil over with steam:—



On this behavior is based Hofmann's mustard oil test for the detection of primary amines (p. 126).

It is advisable to use ferric chloride (*Ber.*, 8, 108) because mercuric chloride will desulphurize the mustard oils and the latter will be transposed into dialkyl ureas. Iodine, too, forms mustard oils from the amine salts of the dithiocarbaminic acids, but the yield is small.

2. By distilling the dialkyl thio-ureas (see these) with phosphorus pentoxide:—

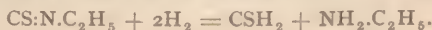


The mustard oils are liquids, almost insoluble in water, and possess a very penetrating odor. They boil at lower temperatures than the isomeric thiocyanic esters.

When heated with hydrochloric acid to  $100^\circ$ , or with  $\text{H}_2\text{O}$  to  $200^\circ$ , they break up into amines, hydrogen sulphide and carbon dioxide:—



On heating with a little dilute sulphuric acid carbon oxysulphide,  $\text{COS}$ , is formed together with the amine. Nascent hydrogen (zinc and hydrochloric acid), acts as follows:—



The mustard oils afford urethanes on heating them with absolute alcohol to  $100^{\circ}$ , or with alcoholic potash. They unite with ammonia and amines, yielding alkylic thio-ureas (see these). Upon boiling their alcoholic solution with  $\text{HgO}$  or  $\text{HgCl}_2$ , a substitution of oxygen for sulphur occurs, with formation of esters of isocyanic acid. These immediately afford the dialkylic ureas with water (see p. 236).

**Methyl Mustard Oil**,  $\text{CS:N.C}_2\text{H}_5$ , methyl isothiocyanic ester, methyl thiocarbimide. It is a crystalline mass, melting at  $34^{\circ}$  and boiling at  $119^{\circ}$ .

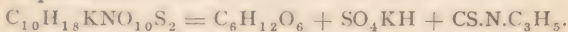
**Ethyl Mustard Oil**,  $\text{CS:N.C}_2\text{H}_5$ , boils at  $133^{\circ}$  and has a specific gravity 1.019 at  $0^{\circ}$ . **Isopropyl Mustard Oil**,  $\text{CS:N.C}_3\text{H}_7$ , boils at  $137^{\circ}$ .

**Butyl Mustard Oil**,  $\text{CS:N.C}_4\text{H}_9$ , (with normal butyl), boils at  $167^{\circ}$ . **Isobutyl Mustard Oil**,  $\text{CS:N.C}_4\text{H}_9$ , (from isobutylamine), boils at  $162^{\circ}$ ; specific gravity 0.9638 at  $14^{\circ}$ . The mustard oil having the secondary butyl group,  $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ , occurs in the ethereal oil of *Cochlearia officinalis*. It boils at  $159.5^{\circ}$ ; its specific gravity equals 0.944 at  $12^{\circ}$ .

**Isoamyl Mustard Oil**,  $\text{CS:N.C}_5\text{H}_{11}$ , boils at  $183^{\circ}$ .

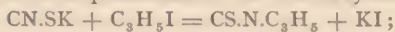
The most important of the mustard oils is the common or—

**Allyl Mustard Oil**,  $\text{CS:N.C}_3\text{H}_5$ —Allyl Thiocarbimide. This is the principal constituent of ordinary mustard oil, which is obtained by distilling powdered black mustard seeds (from *Sinapis nigra*). In the latter there is potassium *myronate* (see Glucosides), which in the presence of water, under the influence of a ferment, *myrosin* (also present in the seed), breaks up into grape sugar, primary potassium sulphate and mustard oil:—



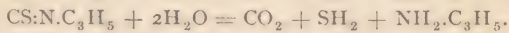
The reaction occurs even at  $0^{\circ}$ , and there is a small amount of allyl sulphocyanate produced at the same time.

Mustard oil is artificially prepared by distilling allyl iodide or bromide with alcoholic potassium or silver thiocyanate:—



a molecular rearrangement occurs here (p. 239).

Pure allyl thiocarbimide is a liquid not readily dissolved by water and boiling at  $150.7^{\circ}$ ; its specific gravity equals 1.017 at  $10^{\circ}$ . It has a pungent odor and causes blisters upon the skin. When heated with water or hydrochloric acid the following reaction ensues:—



It unites with aqueous ammonia to allyl thio-urea. When heated with water and lead oxide it yields diallyl urea.

## CYANIDES OF THE ALCOHOL RADICALS.

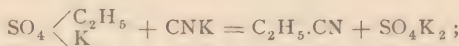
### (1) NITRILES.

By this term we understand those derivatives of the alcohol radicals with the cyanogen group,  $\text{CN}$ , in which the fourth affinity of carbon is linked to the alcohol radicals.



The following general methods serve for their formation :—

1. The distillation of a potassic alkyl sulphate with potassium cyanide :—

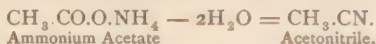


or by heating the alkylogens with potassium cyanide in alcoholic solution to  $100^\circ$  :—



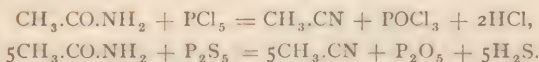
Isocyanides (p. 246) form in slight amount in the first reaction. For their removal shake the distillate with aqueous hydrochloric acid until the unpleasant odor of the isocyanides has disappeared, then neutralize with soda and dry the nitriles with calcium chloride.

2. The dry distillation of ammonium salts of the acids with  $\text{P}_2\text{O}_5$ , or some other dehydrating agent :—



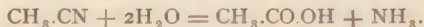
This method of production explains why these cyanides are termed acid nitriles.

3. By the removal of water from the amides of the acids when these are heated with  $\text{P}_2\text{O}_5$ ,  $\text{P}_2\text{S}_5$ —or phosphoric chloride (see amid-chlorides p. 209) :—



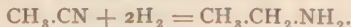
The nitriles occur already formed in bone-oils (*Berichte*, 13, 65).

The nitriles are liquids which are usually insoluble in water, possess an ethereal odor, and distil without decomposition. When heated to  $100^\circ$  with water, they break up into acids and ammonia :—

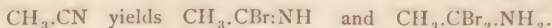


This decomposition is more readily effected on heating with acids or alkalies (p. 168).

Nascent hydrogen (sodium amalgam) converts them into amines :—

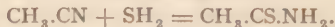


The nitriles can unite directly with bromine and with the halogen hydrides :—



These compounds are identical with those formed by the action of  $\text{PCl}_5$  upon the amides (p. 209).

The nitriles form thio-amides with  $\text{H}_2\text{S}$  (p. 210) :—



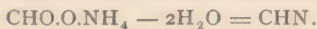
With monobasic acids and acid anhydrides they yield secondary and tertiary amides (p. 208).

With alcohols and HCl they combine to imido-ethers,  $R.C \begin{smallmatrix} \diagup NH \\ \diagdown OR \end{smallmatrix}$  (p. 248); thus, from CNH we get formido-ethers. The nitriles become amidines with ammonia and the amines (p. 249). Metallic sodium induces in them a peculiar polymerization, resulting in the production of bases, like cyanethine (see below).

---

Formonitrile	or	Hydrogen Cyanide,	H.CN
Acetonitrile	"	Methyl	" CH <sub>3</sub> .CN
Propionitrile	"	Ethyl	" C <sub>2</sub> H <sub>5</sub> .CN
Butyronitrile	"	Propyl	" C <sub>3</sub> H <sub>7</sub> .CN
Valeronitrile	"	Butyl	" C <sub>4</sub> H <sub>9</sub> .CN, etc.

1. **Hydrogen Cyanide**, CNH (p. 228), the lowest member of the series, is to be regarded as **formonitrile** because it is obtained from ammonium formate by the withdrawal of water:—



Conversely, on boiling with acids or alkalies it yields formic acid and ammonia. Nascent hydrogen converts it into methylamine, CH<sub>3</sub>.NH<sub>2</sub>.

2. **Acetonitrile, Methyl Cyanide**, CH<sub>3</sub>.CN = C<sub>2</sub>H<sub>3</sub>N, is best obtained by distilling acetamide with P<sub>2</sub>O<sub>5</sub>. It is a liquid with an agreeable odor, and boils at 81.6°. It is miscible with water, and burns with a violet light. When boiled with acids or alkalies it yields ammonia and acetic acid. Nascent hydrogen converts it into ethylamine.

**Cyanmethine**, C<sub>6</sub>H<sub>9</sub>N<sub>3</sub> = C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>(NH<sub>2</sub>), is formed by the action of sodium upon acetonitrile:—



This substance melts at 180°, is readily soluble in water, reacts alkaline and yields salts with one equivalent of the acids. On heating with water or hydriodic acid it breaks up into ammonia and acetic acid. Nitrous acid converts it into the oxy-base, C<sub>6</sub>H<sub>7</sub>(OH)N<sub>2</sub>.

Substituted acetonitriles are obtained from the substituted acetamides by distillation with P<sub>2</sub>O<sub>5</sub>. CH<sub>2</sub>Cl.CN boils at 112°; its specific gravity at 11° equals 1.204. CHCl<sub>2</sub>.CN boils at 112°, and its specific gravity is 1.374 at 11°. CCl<sub>3</sub>.CN boils at 83°; its specific gravity at 12° is 1.439. The direct chlorination of acetonitrile only occurs in the presence of iodine.

3. **Propionitrile, Ethyl Cyanide**, C<sub>3</sub>H<sub>5</sub>N = C<sub>2</sub>H<sub>5</sub>.CN. This is also formed by the action of cyanogen chloride and dicyanogen upon zinc ethyl. It is an agreeably smelling liquid, which boils at 98°. Its specific gravity equals 0.787. Salt separates it from its aqueous solution. In all its reactions, it is perfectly analogous to acetonitrile. It sustains a similar transposition by action of sodium. The resulting **cyanethine**, C<sub>9</sub>H<sub>15</sub>N<sub>3</sub> = C<sub>9</sub>H<sub>13</sub>N<sub>2</sub>(NH<sub>2</sub>), crystallizes in white leaflets, which melt at 189°, and boil with partial decomposition at 280°. It is a mon-acidic base affording crystalline salts with one equivalent of the acids.

When cyanethine is heated to 200° with hydrochloric acid, or on acting on it with nitrous acid, the tertiary base, C<sub>9</sub>H<sub>13</sub>(OH)N<sub>2</sub> forms; this melts at 156°. PCl<sub>5</sub> converts this into the chloride, C<sub>9</sub>H<sub>13</sub>CIN<sub>2</sub>, which alcoholic ammonia trans-

forms into the amide,  $C_9H_{13}(NH_2)N_2$ . This is identical with cyanethine. Nascent hydrogen changes the chloride to the base,  $C_9H_{14}N_2$ , having the composition of conine cyanide, which acts very similar to conine, and hence has been termed *cyanconine*. Cyanethine yields with bromine a bromide derivative, which ammonia converts into isoadic acid. Both an amid- and imid-group are apparently present in cyanethine (*Journ. pr. Chemie*, 26, 337).

Chlorine displaces two hydrogen atoms in propionitrile, yielding  $\alpha$ -dichloropropionitrile,  $CH_3.CCl_2.CN$ . This is a liquid, boiling at  $103-107^\circ$ , and upon standing, it polymerizes to the solid  $(C_3H_3Cl_2N)_3$ . Sodium or sodium amalgam effects the same more rapidly. The product crystallizes in plates, which melt at  $73.5^\circ$ , and decompose when heated. Heated with sulphuric acid and water, both compounds afford  $\alpha$ -dichloropropionic acid, and with alcohol and sulphuric acid its ester (p. 180).

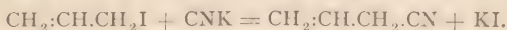
4. **Butyronitrile, Propyl Cyanide**,  $C_3H_7.CN$ , boils at  $118-119^\circ$ , and has the odor of bitter-almond oil. **Isopropyl Cyanide**,  $C_3H_7.CN$ , is formed by the prolonged heating of isobutyric acid with potassium thiocyanate. It boils at  $107-108^\circ$ .

5. **Valeronitriles**,  $C_5H_9.N = C_4H_9.CN$ , **Butyl Cyanides**.

(1) *Normal butyl cyanide* boils at  $140-141^\circ$ ; its specific gravity is 0.816 at  $0^\circ$ . (2) *Isobutyl cyanide* boils at  $126-128^\circ$ , and has the odor of oil of bitter almonds; its specific gravity equals 0.8227 at  $0^\circ$ . (3) *Tertiary butyl cyanide* is produced on heating tertiary butyl iodide,  $(CH_3)_3CI$ , with potassio-mercuric cyanide. It boils at  $105-106^\circ$ , becomes crystalline in the cold, and melts at  $+16^\circ$ .

The following higher nitriles may be easily derived from their respective acid amides by action of  $P_2O_5$ : *Laurenitrile*,  $C_{12}H_{23}N$  (F.P.  $+4^\circ$ ); *myristonitrile*,  $C_{14}H_{27}N$  ( $19^\circ$ ); *palmitonitrile*,  $C_{16}H_{31}N$  ( $31^\circ$ ); and *stearonitrile*,  $C_{18}H_{35}N$  ( $41^\circ$ ).

**Allyl Cyanide**,  $C_3H_5.CN = CH_2:CH.CH_2.CN$ , occurs in crude mustard oil, and is obtained by heating allyl iodide with potassium cyanide:—



It is a liquid with an odor resembling that of leeks, boils at  $117-118^\circ$ , and has a specific gravity of 0.835 at  $15^\circ$ . It yields crotonic acid when boiled with alcoholic potash (p. 192).

## NITRO-DERIVATIVES OF ACETONITRILE.

In this section fall compounds which, although not directly obtained from acetonitrile, are yet regarded as derivatives of it (*Ber.*, 16, 2419).

**Nitro-acetonitrile**,  $C_2H_2N_2O_2 = CH_2(NO_2).CN$ , or hypothetical fulminic acid, is considered the basis of the so-called fulminates, derived from it by the introduction of metals for two hydrogen atoms. The influence of the negative groups, CN and  $NO_2$ , explains the acid nature of nitro-acetonitrile (p. 229).

A compound having the composition of nitro-acetonitrile has been obtained by the action of concentrated sulphuric acid upon ammonium fulminurate. It is a crystalline solid, insoluble in water, melts at  $40^\circ$ , and volatilizes very readily (*Ber.*, 9, 783).

**Mercury Fulminate**,  $C_2HgN_2O_2 = CHg(NO_2).CN(?)$ , is formed by heating a mixture of alcohol, nitric acid and mercuric nitrate.

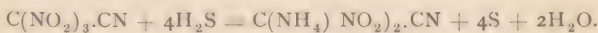
1 part mercury is dissolved in 12 parts nitric acid (sp. gr. 1.345), 5.5 parts alcohol of 90 per cent. added, and the whole well shaken. After a little time, as soon as energetic reaction commences, 6 parts alcohol more are gradually added. At first metallic mercury separates, but subsequently dissolves and deposits as mercuric fulminate in flakes (*Ber.*, 9, 787).

Fulminating mercury crystallizes in shining, gray-colored prisms, which are tolerably soluble in hot water. It explodes violently on percussion and also when acted upon by concentrated sulphuric acid. Hydrogen sulphide precipitates mercuric sulphide from its solution, the liberated fulminic acid immediately breaking up into  $CO_2$  and ammonium thiocyanate. Concentrated hydrochloric acid evolves  $CO_2$  and yields hydroxylamine hydrochloride (*Ber.*, 16, 2419).

Bromine converts mercuric fulminate into *dibromnitroacetonitrile*,  $CBr_2(NO_2).CN$ , which forms large crystals, soluble in alcohol and ether, and melting at  $50^\circ$ . Iodine produces the iodide,  $CI_2(NO_2).CN$ ; colorless prisms, melting at  $86^\circ$ . Chlorine gas changes mercuric fulminate into  $HgCl_2$ ,  $CNCl$  and chloropicrin. Ammonia in aqueous solution decomposes it into urea and guanidine.

On boiling mercury fulminate with water and copper or zinc, metallic mercury is precipitated and copper and zinc fulminates ( $C_2CuN_2O_2$  and  $C_2ZnN_2O_2$ ) are produced. Silver fulminate,  $C_2Ag_2N_2O_2$ , is prepared after the manner of the mercury salt, and resembles the latter. Potassium chloride precipitates from hot silver fulminate one atom of silver as chloride and the double salt,  $C_2AgKN_2O_2$ , crystallizes from the solution. Nitric acid precipitates from this salt *acid silver fulminate*,  $C_2AgHN_2O_2$ , a white, insoluble precipitate.

**Dinitro acetonitrile**,  $CH(NO_2)_2.CN$ . Its ammonium salt is produced when hydrogen sulphide acts upon *trinitro acetonitrile* :—



Sulphuric acid liberates the nitrile from this salt, and it may be withdrawn from the solution by shaking with ether. It forms large, colorless crystals, and conducts itself like a monobasic acid. The silver salt,  $C_2Ag(NO_2)_2N$ , explodes very violently. It forms  $C_2Br(NO_2)_2N$  with bromine.

**Trinitro-acetonitrile**,  $C_2(NO_2)_3N$ , is obtained by the action of a mixture of concentrated nitric and sulphuric acids upon potassium fulminate. It separates out as a thick oil, with evolution of  $CO_2$ , and on cooling solidifies.

Trinitro-acetonitrile is a white, crystalline, camphor-like mass, melting at  $41.5^\circ$ , and exploding at  $200^\circ$ . It volatilizes at  $60^\circ$  in an air current. Water and alcohol decompose it, even in the cold, into  $CO_2$  and the ammonium salt of nitroform (p. 83).

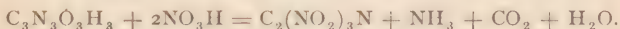
**Fulminuric Acid**,  $C_3N_3O_3H_3$ , or Isocyanuric Acid. Its alkali salts are obtained by boiling mercuric fulminate with potassium chloride or ammonium chloride and water. In its preparation 60–75 grains of mercuric fulminate are heated with 60 c.c. of a saturated ammonium chloride solution, and 700–800 c.c. of water, until mercuric oxide no longer separates. The solution will then contain  $HgCl_2$  and ammonium fulminurate. Ammonium hydrate is now employed to throw out all the mercury, when the solution is filtered and concentrated to



crystallization. To obtain the free acid, add lead acetate to the solution of the ammonium salt, decompose the lead salt with hydrogen sulphide and evaporate the filtrate down to a small bulk.

Fulminuric acid is an indistinctly crystalline mass, soluble in water, alcohol and ether, and deflagrating at  $145^{\circ}$ . It is a monobasic acid, yielding finely crystallized alkali salts. Especially characteristic is the *Cuprammonium salt*,  $C_3N_3O_3H_3$  ( $CuNH_3$ ), which precipitates from the aqueous solution of the acid or its alkali salt when boiled with ammoniacal copper sulphate. It consists of glistening dark blue prisms. Mercury fulminurate is produced when mercury fulminate is heated with alcoholic ammonia.

Trinitroacetonitrile is formed by the action of a mixture of concentrated nitric and sulphuric acids upon fulminuric acid:—

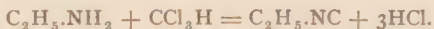


The constitution of fulminuric acid is not known.

## (2) ISOCYANIDES OR CARBYLAMINES.

These constitute a series of compounds parallel to, and isomeric with, the nitriles or alkylcyanides. They are obtained:—

1. By heating chloroform and primary amines with alcoholic potash (A. W. Hofmann):—



The carbylamine test of Hofmann for detection of primary amines is based on this (p. 126).

2. By action of the alkyl iodides upon silver cyanide (p. 231) (Gautier):—



*Preparation.*—Heat 2 molecules of silver cyanide with 1 molecule of the iodide, diluted with  $\frac{2}{3}$  volume of ether, in sealed tubes to  $130^{\circ}$ – $140^{\circ}$  for several hours. Water and potassium cyanide ( $\frac{1}{2}$  part) are added to the product (a compound of the isocyanide with silver cyanide) and the whole distilled upon a water bath.

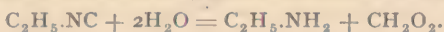
3. The isonitriles are produced, too, in the preparation of the nitriles from alkyl sulphates and potassium cyanide (p. 242).

The carbylamines are colorless liquids which can be distilled, and possess an exceedingly disgusting odor. They are difficultly soluble in water, but readily soluble in alcohol and ether.

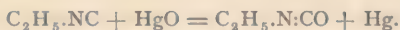
While, in the nitriles, the carbon of the cyanogen group is firmly attached to the alcohol radicals, and nitrogen splits off readily as  $NH_3$ , in all decomposition reactions of the isonitriles nitrogen remains in combination with the alcohol radical. Hence, in the latter we assume the presence of the isomeric *isocyanogen group*, in which nitrogen figures as a pentad:—



The isocyanides are characterized by their ready decomposition by dilute acids, upon which they split into formic acid and amines :—



The same decomposition occurs when they are heated with  $\text{H}_2\text{O}$  to  $180^\circ$ . When oxidized by mercuric oxide they become isocyanic esters (p. 236) :—



Like the cyanides, the isocyanides form crystalline compounds with  $\text{HCl}$ , which are broken up by water into formic acid and amine bases (p. 242). They pass into thio-formamides by their union with  $\text{H}_2\text{S}$  (p. 210).

**Methyl Isocyanide**,  $\text{CH}_3.\text{NC}$ , methyl carbylamine, boils at  $59^\circ$  and dissolves in 10 parts of water. When heated with water it decomposes.

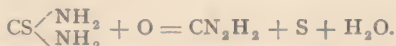
**Ethyl Isocyanide**,  $\text{C}_2\text{H}_5.\text{NC}$ , is an oily liquid which swims upon water and boils at  $79^\circ$ .

**Isoamyl Isocyanide**,  $\text{C}_5\text{H}_{11}.\text{NC}$ , boils at  $137^\circ$  and swims on water.

**Allyl Isocyanide**,  $\text{C}_3\text{H}_5.\text{NC}$ , boils near  $106^\circ$ , and has a specific gravity of 0.796 at  $17^\circ$ .

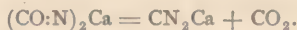
## AMIDE DERIVATIVES OF CYANOGEN.

**Cyanamide**,  $\text{CN}.\text{NH}_2$ , or carbodiimide,  $\text{C}(\text{NH})_2$ , is formed by the action of an ethereal ammonia solution upon chlor- or brom-cyan, by the action of carbon dioxide upon sodium amide ( $\text{NH}_2\text{Na}$ ), and also by the desulphurizing of thio-urea by means of mercuric chloride or lead peroxide :—



It forms colorless crystals, easily soluble in water, alcohol and ether, and melting at  $40^\circ$ . An ammoniacal silver nitrate solution throws down a yellow precipitate,  $\text{CN}_2\text{Ag}_2$ , from its solutions. Copper sulphate precipitates black  $\text{CN}_2\text{Cu}$ .

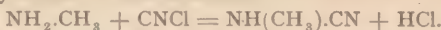
Such metallic compounds are obtained directly by heating the salts of isocyanic acid with the alkaline earths and the heavy metals :—



On this fact is based the method of preparing cyanamide by igniting a mixture of potassium isocyanate and calcium chloride (*Ber.*, 13, 570).

The various transpositions of the above compound do not determine whether we should consider it as cyanamide or carbodiimide,  $\text{C}(\text{NH})_2$ . By the action of sulphuric acid, phosphoric acid or nitric acid, it absorbs water and becomes urea.  $\text{H}_2\text{S}$  converts it into thio-urea, and  $\text{NH}_3$  into guanidine (p. 250).

*Alkyl cyanamides* or *Carbodiimides* are obtained by letting cyanogen chloride act upon primary amines in ethereal solution :—



They may be prepared also by heating the corresponding thio-ureas with mercuric oxide and water :—



**Methyl Cyanamide**,  $\text{CN}_2\text{H}(\text{CH}_3)$ , and **Ethyl Cyanamide**,  $\text{CN}_2\text{H}(\text{C}_2\text{H}_5)$ , are non-crystallizable thick syrups with neutral reaction. They are readily converted into polymeric cyanuramide (melamine) derivatives.

**Allyl Cyanamide**,  $\text{CN}_2\text{H}(\text{C}_3\text{H}_5)$ , is obtained from allylthiourea. It passes readily into triallylmelamine (see below.)

**Dicyanamide**,  $\text{NH}(\text{CN})_2$ , is only known in its salts. The *potassium salt*,  $\text{C}_2\text{N}_3\text{K}$ , is obtained by heating potassium cyanide with paracyanogen or with mercuric cyanide (*Ber.*, 13, 2202). It crystallizes in thin needles. Silver nitrate precipitates a white silver salt,  $\text{C}_2\text{N}_3\text{Ag}$ , from its solution.

**Dicyandiamide**,  $\text{C}_2\text{N}_4\text{H}_4$ , *Param*, results from the polymerization of cyanamide upon long standing or by evaporation of its aqueous solution. It crystallizes in leaflets which melt at  $205^\circ$ . It is insoluble in ether. Its structure probably agrees with the formula,  $\text{NH}:\text{C} \begin{array}{c} \text{NH}_2 \\ \text{NH}\cdot\text{CN} \end{array}$ . Hence, it can be called cyanguanidine (*Ber.*, 16, 1464).

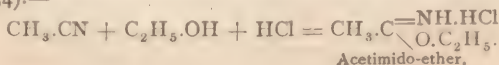
**Dicyandiamidine**,  $\text{C}_2\text{H}_6\text{N}_4\text{O} = \text{NH}:\text{C} \begin{array}{c} \text{NH}_2 \\ \text{NH}\cdot\text{CO}\cdot\text{NH}_2 \end{array}$  (guanyl urea), is formed by the action of dilute acids upon dicyandiamide or cyanamide, or by fusing a guanidine salt with urea. It is a strongly basic, crystalline substance. When its aqueous solution is evaporated in the air it decomposes into  $\text{CO}_2$ ,  $\text{NH}_3$  and guanidine.

By boiling dicyandiamide with baryta water it is converted into **Amido-dicyanic acid**,  $\text{CO} \begin{array}{c} \text{NH} \\ \text{NH} \end{array} \text{C}:\text{NH}$ . This crystallizes in needles, and when heated with sulphuric acid changes to biuret.

A derivative of tri-isocyanic acid or isocyanuric (p. 234) acid, similar to dicyanamide, is **Melamine**,  $\text{C}_3\text{N}_6\text{H}_6 = \text{C}_3\text{N}_3\text{H}_3(\text{NH})_3(?)$ . This results from the polymerization of cyanamide,  $\text{CN}_2\text{H}_2$ , when heated to  $150^\circ$ . It crystallizes from hot water in large rhombic octahedra, and affords salts with 1 equivalent of the acids; these crystallize well. On boiling with alkalis or acids it is converted successively into **Ammeline**,  $\text{C}_3\text{N}_5\text{OH}_5 = \text{C}_3\text{N}_3\text{H}_3\text{O}(\text{NH})_2$ , **Ammelide**,  $\text{C}_3\text{N}_4\text{O}_2\text{H}_4 = \text{C}_3\text{N}_3\text{H}_3\text{O}_2(\text{NH})$ , and finally isocyanuric acid,  $\text{C}_3\text{N}_3\text{O}_3\text{H}_3$ . Potassium isocyanurate is immediately produced on heating it with potassium hydroxide.

The imido-ethers, the amidines and guanidine (p. 250), are intimately related to the nitriles and cyanamides.

The **Imido-Ethers**,  $\text{R}\cdot\text{C} \begin{array}{c} \text{NH} \\ \text{OR} \end{array}$  (their  $\text{HCl}$  salts), are produced by the action of  $\text{HCl}$  upon a mixture of a nitrile with an alcohol (in molecular quantities) (*Ber.*, 16, 353, 1654):—



**Acetimido-ethyl Ether**, when liberated from its HCl salt by means of NaOH, is a peculiar-smelling liquid, boiling at  $97^{\circ}$ . Its HCl-salt crystallizes in shining leaflets, and like the other imido-ethers is readily decomposed by heat (with formation of acetamide and ethyl chloride).

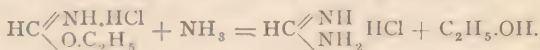
The *formimido-ethers* are obtained from CNH, alcohol and HCl by a reaction analogous to that given above :—



These are only known in their salts, which suffer various noteworthy transformations. Upon standing with alcohols they pass into esters of orthoformic acid (see this) :—



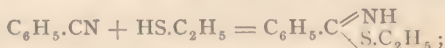
They yield amidines with ammonia and amines (primary and secondary) :—



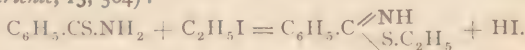
All the other imido-ethers react similarly. With hydroxylamine they yield the *acidoxims* (*Berichte*, 17, 185), corresponding to the aldoxims and acetoxims :—



Corresponding to the imido-ethers are the *imido-thio-ethers*. They are obtained by the action of HCl upon nitriles (of the benzene series), and mercaptans :—



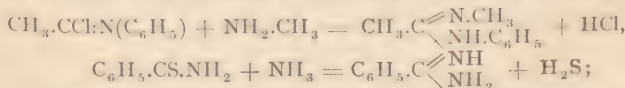
further, when the *thio-amides* (of the benzene series), are treated with alkyl-iodides (*Berichte*, 15, 564) :—



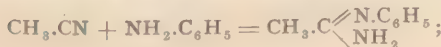
This class of compounds has a constitution similar to that of the isothio-amides (p. 210).

The *amidines*,  $\text{R.C} \begin{array}{l} \diagup \text{NH} \\ \diagdown \text{NH}_2 \end{array}$ , whose hydrogen atoms can be replaced by alkyls, are produced :—

1. From the imid-chlorides, thio-amides, and isothio-amides (p. 210) (*Berichte*, 16, 146), by the action of ammonia or amines (primary and secondary) :—

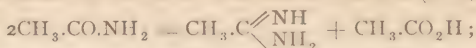


2. From the nitriles by heating them with ammonium chloride or HCl-amines :—



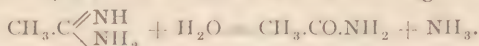


3. From the amides of the acids when treated with HCl (*Ber.*, 15, 208):—



4. From the imido-ethers (p. 248) when acted upon with ammonia and amines (*Ber.*, 16, 1647, 17, 179).

The amidines are mono-acid bases. In a free condition they are quite unstable. The action of various reagents on them induces water absorption, the imid-group splits off, and acids or amides of the acids are regenerated:—



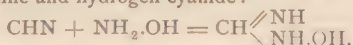
$\text{H}_2\text{S}$  causes the elimination of the imid- or amid-group from the amidines, and thus converts them into thio-amides (p. 209).  $\text{CS}_2$  effects the same, sulphocyanic acid,  $\text{CNSH}$ , and mustard oils,  $\text{CS}\cdot\text{NR}$ , being simultaneously produced (*Ann.*, 192, 30). Acetic anhydride causes them to pass through various transpositions (*Ber.*, 17, 176). Hydroxylamine supplants the imid-group in them with the oximid-group,  $\text{N}\cdot\text{OH}$ , with formation of oxamidines,  $\text{R}\cdot\text{C} \begin{array}{c} \text{N}\cdot\text{OH} \\ \diagup \quad \diagdown \\ \text{NH}_2 \end{array}$  (*Ber.*, 17, 185).

**Formamidine**,  $\text{CN}_2\text{H}_4 = \text{CH} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH}_2 \end{array}$  (**Methenylamidine**), is only known in its salts. The HCl-salt,  $\text{CN}_2\text{H}_4\cdot\text{HCl}$ , is obtained from  $\text{CNH}\cdot\text{HCl}$  (p. 229) on heating it with alcohol:—



It consists of very hygroscopic needles, melting at  $81^\circ$ , and is decomposed into  $\text{NH}_3$  and formic acid by the alkalis.

**Isuret**,  $\text{CON}_2\text{H}_4 = \text{CH} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH}\cdot\text{OH} \end{array}$  (isomeric with urea). This is an hydroxyl derivative of formamidine. It appears on evaporating the alcoholic solution of hydroxylamine and hydrogen cyanide:—



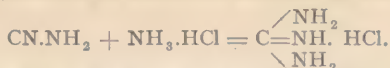
It crystallizes in rhombic prisms, similar to those of urea, and melts with partial decomposition at  $104^\circ$ – $105^\circ$ . It reacts alkaline and forms crystalline salts with 1 equivalent of the acids. On heating the solutions of its salts, the latter decompose into formic acid, ammonia and hydroxylamine. When isuret, in aqueous solution, is boiled, it breaks up into nitrogen,  $\text{CO}_2$ ,  $\text{NH}_2$ , guanidine, urea and biuret.

**Acetamidine**,  $\text{C}_2\text{H}_6\text{N}_2 = \text{CH}_3\cdot\text{C} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH}_2 \end{array}$  (**Acediamine**), is obtained by heating acetamide in a stream of HCl. Its hydrochloric acid salt crystallizes in large, shining prisms that melt at  $165^\circ$ . The acetamidine, separated by alkalis, reacts strongly alkaline and readily breaks up into  $\text{NH}_3$  and acetic acid. The higher amidines and their alkyl derivatives are easily obtained by the usual methods (*Ber.*, 17, 178).

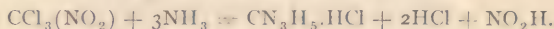
The so-called anhydro-bases and ethenyl derivatives of the benzene series (see these) also belong with the amidines.

**Guanidine**,  $\text{CN}_3\text{H}_5 = \text{HN}:\text{C} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NH}_2 \end{array}$  carb-diamid-imide, was first obtained by the oxidation of guanine with hydrochloric acid and potassium chlorate, hence, its name. It is formed synthetically

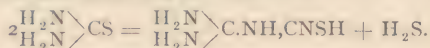
by heating cyanogen iodide and  $\text{NH}_3$ , and from cyanamide (p. 247) and ammonium chloride in alcoholic solution at  $100^\circ$ :—



It is also produced by heating chloropicrin or esters of ortho-carbonic acid, with aqueous ammonia, to  $150^\circ$ :—



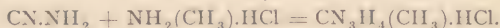
It is most readily prepared from the sulphocyanate salt, which is made by prolonged heating of ammonium sulphocyanate to  $180^\circ$ – $190^\circ$ , and the further transposition of the thio-urea that forms at first:—



To get the free guanidine from this salt, evaporate the aqueous solution with an equivalent quantity of potassium carbonate, extract the potassium thio-cyanate from the mass with boiling alcohol, and convert the residual guanidine carbonate into sulphate, and from this liberate the guanidine by means of baryta (*Ber.*, 7, 92).

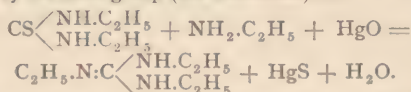
The crystals of guanidine are very soluble in water and alcohol, and deliquesce on exposure. It is a strong base, absorbing  $\text{CO}_2$  from the air and affording crystalline salts with 1 equivalent of the acids. The nitrate,  $\text{CN}_3\text{H}_5.\text{HNO}_3$ , consists of large scales, which are difficultly soluble in water. The HCl-salt,  $\text{CN}_3\text{H}_5.\text{HCl}$ , yields a platinum double salt, crystallizing in yellow needles. The carbonate,  $(\text{CN}_3\text{H}_5)_2.\text{H}_2\text{CO}_3$ , consists of quadratic prisms, and reacts alkaline. The sulphocyanate,  $\text{CN}_3\text{H}_5.\text{HSCN}$ , crystallizes in large leaflets, that melt at  $118^\circ$ .

The *substituted guanidines* resulting from the introduction of alcohol radicals, are obtained by reactions analogous to those employed in the preparation of guanidine, viz., the heating of cyanamide with the HCl-salts of the primary amines:—



**Methyl Guanidine**,  $\text{CN}_3\text{H}_4(\text{CH}_3)$ . Silver oxide separates this from the HCl salt. It forms a deliquescent, crystalline mass. Its salts with 1 equivalent of acid crystallize quite well. It is also produced on boiling creatine with mercuric oxide and water.

**Triethyl Guanidine**,  $\text{CN}_3\text{H}_2(\text{C}_2\text{H}_5)_3$ , is obtained by boiling diethyl thio-urea and ethylamine in alcoholic solution with mercuric oxide, whereby sulphur is directly replaced by the imid-group (see thio-ureas):—



*Vice versa*, the alkyl guanidines, when heated with  $\text{CS}_2$ , have their imid-group replaced by sulphur (same as with the amidines, p. 250), with formation of thio-ureas.

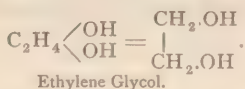
The guanidine-benzene derivatives are especially numerous. Acid residues may also replace the hydrogen of guanidine; these derivatives will receive attention when the urea compounds are described.

Guanidine also forms salts with the fatty acids. When these are heated to 220–230°, water and ammonia break off, and the **guanamines** result. These are produced by the union of 1 molecule of acid and 2 molecules of guanidine. They are mono-acids, and very probably have a structure similar to that of the amidines (p. 248). Here belong *formo-guanamine*,  $C_3H_5N_5$ , from guanidine formate, *aceto-guanamine*,  $C_4H_7N_5$ , from the acetate, *propio-guanamine*,  $C_5H_9N_5$ , *butyro-* and *isobutyro-guanamine*,  $C_6H_{11}N_5$ , etc. (*Ber.*, 9, 454).

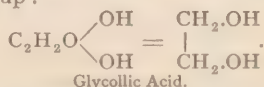
## DIVALENT COMPOUNDS.

The introduction of *two* monovalent groups into the hydrocarbons for two hydrogen atoms affords us the divalent compounds.

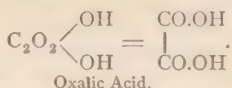
The replacement of hydrogen by two hydroxyl groups yields the divalent *alcohols* or *glycols*, which we can also term dialcohols (see p. 86):—



By replacing two hydrogen atoms in the glycols by oxygen, we get the *divalent* (dihydric) *monobasic acids*, containing one carboxyl and one hydroxyl group:—



The substitution of two additional hydrogen atoms by oxygen yields the *divalent, dibasic acids*, with two carboxyl groups:—



Numerous related derivatives attach themselves to these three principal groups of divalent compounds.

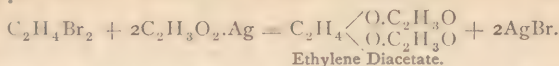
We can in a broader sense include under divalent compounds all bodies of double and mixed function, such as the ketone alcohols and ketonic acids (p. 214) and the diketones (p. 200). To them belong also the aldehyde-alcohols like aldol,  $C_3H_6 \begin{matrix} \diagup OH \\ \diagdown CHO \end{matrix}$ , the dialdehydes, like glyoxal,  $CHO.CHO$ , the aldehyde acids, as glyoxylic acid,  $CHO.CO_2H$ , etc., etc. But few such compounds are known at present, therefore we will study them in connection with the substances with which they are related.

## DIVALENT (DIHYDRIC) ALCOHOLS OR GLYCOLS.

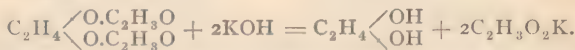
Würtz obtained the glycols in 1856, from the haloid compounds of the alkylens,  $C_nH_{2n}$ . They are formed as follows:—

1. By heating the alkylen haloids (p. 71) with silver acetate

(and glacial acetic acid), or with potassium acetate in alcoholic solution:—

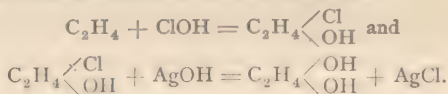


The resulting acetic esters are purified by distillation, and then saponified by KOH:—

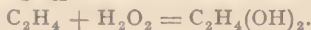


Generally in using potassium acetate, a mixture of di-acetate and mono-acetate is produced with free glycol. The mixture is saponified with KOH, or  $\text{Ba}(\text{OH})_2$ . A direct conversion of alkylens haloids into glycols may be attained by heating them with water and lead oxide, or sodium and potassium carbonate (p. 89). When ethylene bromide is heated for some time with much water above  $100^\circ$  it is completely changed to ethylene glycol, whereas with little water aldehyde results (*Ann.*, 186, 393).

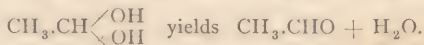
2. Another procedure consists in shaking the alkylens,  $\text{C}_n\text{H}_{2n}$ , with aqueous hypochlorous acid, and afterwards decomposing the chlorhydrins formed with moist silver oxide:—



The glycols appear in small quantities when hydrogen peroxide acts on the olefines  $\text{C}_n\text{H}_{2n}$ :—

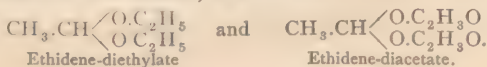


From the method of producing glycols out of the alkylens,  $\text{C}_n\text{H}_{2n}$ , by means of their addition products, it would appear that in the glycols the hydroxyl groups are bound to *two different* carbon atoms. One carbon atom can link but *one* OH group. Thus from ethidene chloride,  $\text{CH}_3\cdot\text{CHCl}_2$ , we cannot obtain the corresponding glycol,  $\text{CH}_3\cdot\text{CH}(\text{OH})_2$ . When dihydroxides do form, water separates and the corresponding anhydrides—the aldehydes (p. 149)—result:—



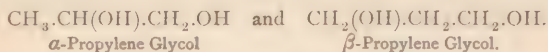
The union of two OH groups to one carbon atom is more stable if the neighboring carbon atom be attached to negative elements. Thus the rather stable hydrate of chloral,  $\text{CCl}_3\cdot\text{CHO} + \text{H}_2\text{O}$ , can be viewed as a dihydroxyl derivative (as tri-chlorethidene glycol),  $\text{CCl}_3\cdot\text{CH} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$  (compare glyoxylic and mesoxalic acids). Such hydroxyl groups are usually not capable of further exchange, as is the case with those in the glycols.

While, therefore, the union of two hydroxyl groups to one carbon atom is but feeble, two oxygen atoms may be firmly attached, if they are linked at the same time with alcoholic or acid radicals, as in





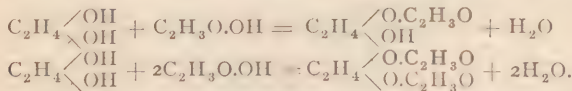
The possible isomerisms for the glycols are deduced from the corresponding hydrocarbons, according to the ordinary rules, with the single limitation that but one OH group can be attached to each carbon atom. Thus two glycols  $C_3H_6(OH)_2$  are derived from propane :—



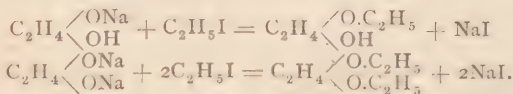
The first contains both a primary and a secondary alcohol group (p. 88), and therefore can be called *primary-secondary glycol*; the second has two primary alcoholic groups, and represents a *di-primary glycol*, etc. The higher glycols are similarly named.

The glycols are neutral, thick liquids, holding, as far as their properties are concerned, a place intermediate between the monohydric alcohols and trihydric glycerol. The solubility of a compound in water increases according to the accumulation of OH groups in it, and it will be correspondingly less soluble in alcohol, and especially in ether. There will be also an appreciable rise in the boiling temperature, while the body acquires at the same time a sweet taste, inasmuch as there occurs a gradual transition from the hydrocarbons to the sugars. In accord with this, the glycols have a sweetish taste, are very easily soluble in water, slightly soluble in ether, and boil much higher (about  $100^\circ$ ) than the corresponding monohydric alcohols.

The hydrogen of the hydroxyls may be replaced by the alkali metals (with formation of metallic glycollates, p. 96), and by acid and alcohol radicals. The acid esters are produced by the action of the salts of the fatty acids upon haloid compounds of the alkyls, or even when the free acids act on the glycols (p. 203):—

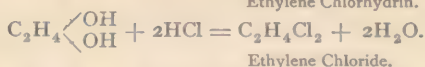
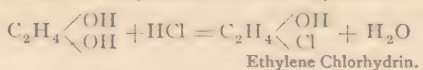


The *alcohol-ethers* are obtained from the metallic glycollates by the action of the alkyl iodides:—



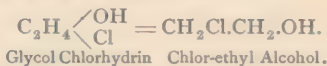
When the glycols are treated with hydrochloric and hydrobromic acid, the primary and secondary *haloid esters* (p. 114) are produced.

The former are also called chlor- and brom-hydrins, while the latter represent the halogen compounds of the alkylens :—

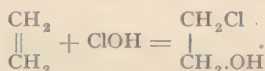


When heated with HI, a more extensive reaction occurs (p. 67).

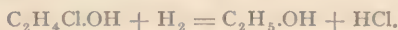
The primary haloid esters can also be considered as substitution products of the monohydric alcohols :—



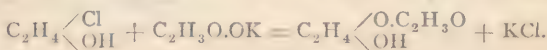
They can be obtained, too, by the direct addition of hypochlorous acid to the alkylens :—



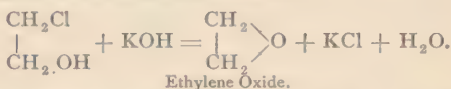
Nascent hydrogen converts them into monohydric alcohols :—



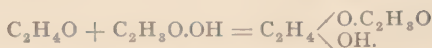
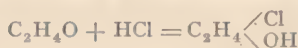
When they are digested with salts they form primary esters :—



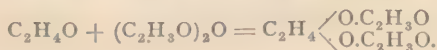
By treating the haloidhydrins with alkalis we obtain the *anhydrides* of the glycols or *alkylen oxides* :—



Such oxides, having the oxygen attached to two carbon atoms, are isomeric with the aldehydes and ketones, and boil at lower temperatures than the latter. Notwithstanding they show neutral reaction, they yet possess a strong basic character, precipitating metallic hydroxides from solutions of metallic salts and uniting themselves with acids to form primary esters of the glycols :—



With the acid anhydrides they yield secondary esters of the glycols :—



The alkylen oxides are readily soluble in water (distinction from alkyl oxides or esters). When they are heated with water the glycols are regenerated (*Berichte*, 16, 397).

Like the monohydric alcohols, the glycols also afford sulphur compounds, amines and sulphonic acids.

#### *Methylene Derivatives.*

**Methylene Glycol**,  $\text{CH}_2(\text{OH})_2$ , is not known and cannot exist (p. 253). Wherever it should occur it eliminates water and yields methylene oxide (*i. e.*, formaldehyde), and trioxymethylene (p. 153.) Its ethers and esters have been prepared.

**Methylene Diacetic Ester**,  $\text{CH}_2(\text{O.C}_2\text{H}_3\text{O})_2$ , is produced on heating methylene iodide with silver nitrate. An oily liquid, insoluble in water and boiling at  $170^\circ$ . Boiling alkalis saponify it, but instead of affording the expected methylene glycol, trioxymethylene is produced.

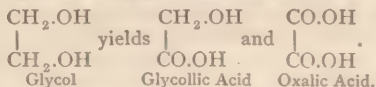
**Methylene Dimethyl Ether**,  $\text{CH}_2(\text{O.CH}_3)_2$ , *Methylal* or *Formal*, is obtained in the oxidation of methyl alcohol with  $\text{MnO}_2$  and sulphuric acid. It is an ethereal liquid of specific gravity 0.855, and boils at  $42^\circ$ . It is miscible with alcohol and ether, and dissolves in 3 parts water. The *diethyl ether*,  $\text{CH}_2(\text{O.C}_2\text{H}_5)_2$ , is prepared by the action of sodium ethylate upon methylene chloride,  $\text{CH}_2\text{Cl}_2$ , or by distilling trioxymethylene with alcohol and sulphuric acid. It boils at  $89^\circ$ .

#### 1. Ethylene Glycol, $\text{C}_2\text{H}_6\text{O}_2 = \text{C}_2\text{H}_4(\text{OH})_2$ .

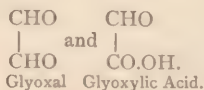
This is a colorless, thick liquid, with a specific gravity of 1.125 at  $0^\circ$ , and boiling at  $197.5^\circ$ . It is miscible with water and alcohol. Ether dissolves but small quantities of it.

*Preparation.*—1. Heat a mixture of 195 grams ethylene bromide (1 molecule), 102 grams potassium acetate (2 molecules), and 200 grams alcohol, of 90 per cent., until all the ethylene bromide is dissolved, then filter off the potassium bromide and fractionate the filtrate (*Demote*). 2. Boil 188 grams ethylene bromide, 138 grams  $\text{K}_2\text{CO}_3$  and 1 litre of water, until all the ethylene bromide is dissolved (*Annalen*, 192, 240 and 250).

On heating ethylene glycol with zinc chloride water is eliminated and acetaldehyde (and crotonaldehyde) (p. 103) formed. Nitric acid oxidizes glycol to glycollic and oxalic acids:—



The following aldehyde-compounds are produced at the same time:—



And when glycol is heated, together with caustic potash, to  $250^\circ$ , it is oxidized to oxalic acid with evolution of hydrogen.

Heated to  $200^{\circ}$  with concentrated hydrochloric acid, glycol is converted into ethylene chloride,  $C_2H_4Cl_2$ .

Metallic sodium dissolves in glycol, forming sodium mono-ethylenate  $C_2H_4 \begin{smallmatrix} \diagup OH \\ \diagdown ONa \end{smallmatrix}$ , and (at  $170^{\circ}$ ) disodium ethylenate,  $C_2H_4(ONa)_2$ . Both are, white, crystalline bodies, regenerating glycols with water. The alkylogens convert them into ethers.

**Ethylene Ethyl Ether**,  $C_2H_4 \begin{smallmatrix} \diagup OHI \\ \diagdown O.C_2H_5 \end{smallmatrix}$ , is formed by the union of ethylene oxide with ethyl alcohol. A pleasantly smelling liquid, boiling at  $127^{\circ}$ .

**Ethylene Diethyl Ether**,  $C_2H_4(O.C_2H_5)_2$ , is insoluble in water, and boils at  $123^{\circ}$ .

The following acid esters have been made:—

**Glycol Mono-acetate**,  $C_2H_4 \begin{smallmatrix} \diagup O.C_2H_3O \\ \diagdown OHI \end{smallmatrix}$ , boils at  $182^{\circ}$ , and is miscible with water.

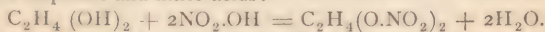
If hydrochloric acid gas be conducted into the warmed solution, **glycol chlor-acetin**,  $C_2H_4 \begin{smallmatrix} \diagup O.C_2H_3O \\ \diagdown Cl \end{smallmatrix}$ , or chlorinated acetic ethyl ester,  $CH_2Cl.CH_2.O.C_2H_3O$ , is produced. This boils at  $144^{\circ}$ .

**Glycol Diacetate**,  $C_2H_4(O.C_2H_3O)_2$ , is obtained by heating ethylene bromide with silver acetate. A liquid of specific gravity 1.128 at  $0^{\circ}$ , and boiling at  $186^{\circ}$ . It is soluble in 7 parts water.

**Glycol or Ethylene Chlorhydrin**,  $CH_2Cl.CH_2.OH$  (p. 255), is formed by heating glycol to  $160^{\circ}$ , and conducting  $HCl$  through it, or by the addition of  $ClOH$  to  $C_2H_4$ . It is a liquid, boiling at  $128^{\circ}$ , and is miscible with water. A chromic acid mixture oxidizes it to monochlor-acetic acid,  $CH_2Cl.CO_2H$ . **Ethylene bromhydrin**,  $C_2H_4Br.OH$ , is not very soluble in water, and boils at  $147^{\circ}$ ; its specific gravity at  $8^{\circ}$  equals 1.66. When chlorhydrin is heated with potassium iodide we get **glycol iodhydrin**,  $C_2H_4I.OH$ . This is a thick liquid, which decomposes when distilled.

**Glycol or Ethylene-hydroxy-sulphuric Acid**,  $C_2H_4 \begin{smallmatrix} \diagup OHI \\ \diagdown O.SO_2.OH \end{smallmatrix}$ , is produced on heating glycol with sulphuric acid. It is perfectly similar to ethyl sulphuric acid (p. 117), and decomposes, when boiled with water or alkalis, into glycol and sulphuric acid.

**Ethylene Nitrate**,  $C_2H_4(O.NO_2)_2$ , is produced on heating ethylene iodide with silver nitrate in alcoholic solution, or by dissolving glycol in a mixture of concentrated sulphuric and nitric acids:—



*This reaction is characteristic of all hydroxyl compounds (the polyhydric alcohols and polyhydric acids); the hydrogen of hydroxyl is replaced by the  $NO_2$  group.*

The nitrate is a yellowish liquid, insoluble in water, and has a specific gravity of 1.483 at  $8^{\circ}$ . It explodes when heated (like the so-called nitroglycerol). The alkalis saponify the esters with formation of nitric acid and glycol.

**Ethylene Cyanide**,  $C_2H_4(CN)_2$ , is obtained on heating an alcoholic solution of ethylene bromide and potassium cyanide, and in the electrolysis of cyanacetic acid. It forms a crystalline mass, fusing at  $54.5^{\circ}$ . Boiled with acids or alkalis, it passes into succinic acid, hence may be looked upon as the nitrile of the latter (p. 241). Nascent hydrogen converts it into butylene diamine,  $C_4H_8(NH_2)_2$ .

**Ethylene Oxide**,  $C_2H_4O = \begin{smallmatrix} CH_2 \\ \diagdown \\ CH_2 \end{smallmatrix} O$ , is isomeric with acetaldehyde, and is produced on distilling ethylene chlorhydrin or



ethylene chloracetin with caustic potash. A mobile, pleasantly smelling, ethereal liquid, which boils at  $13.5^{\circ}$ , and at  $0^{\circ}$  has a specific gravity equal to 0.898. It is miscible with water, gradually combining with it to form ethylene glycol.

The oxide possesses strong basic properties, precipitating the heavy metals as hydroxides from solutions of their salts, and combining with acids to yield esters (p. 254).

It combines with bromine, forming a crystalline, red *bromide*,  $(C_2H_4O)_2Br$ , which melts at  $65^{\circ}$ , and distils at  $95^{\circ}$ . Mercury changes the bromide to *diethylene*

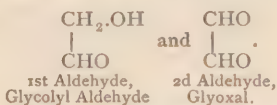
*oxide*,  $(C_2H_4O)_2$   $\begin{array}{c} CH_2-O-CH_2 \\ | \quad \quad | \\ CH_2-O-CH_2 \end{array}$ . This melts at  $9^{\circ}$ , and distils at  $102^{\circ}$ . It combines with acetaldehyde to form *ethylene-ethylidene ether*,  $C_2H_4 \begin{array}{c} \diagup O \\ \diagdown O \end{array} CH_3$ , which boils at  $82.5^{\circ}$ .

**Ethylene Thiohydrate**,  $C_2H_4 \begin{array}{c} \diagup SH \\ \diagdown SH \end{array}$ , glycol mercaptan, is formed on heating an alcoholic solution of potassium sulphhydrate with ethylene bromide. The odor of this compound is something like that of mercaptan. It boils at  $146^{\circ}$ ; its specific gravity is 1.12. Insoluble in water, it dissolves in alcohol and ether. Acids reprecipitate it from alkaline solutions. It throws out mercaptides, *e. g.*,  $C_2H_4.S_2Pb$ , from the salts of the heavy metals.

The **monothiohydrate**,  $C_2H_4 \begin{array}{c} \diagup SH \\ \diagdown OH \end{array}$ , is obtained when ethylene chlorhydrin acts on potassium sulphhydrate. It yields mercaptides with 1 equivalent of the metals.

**Ethylene Sulphide**,  $C_2H_4S$ —isomeric with thioaldehyde,  $CH_3.CHS$ .—is formed on heating ethylene bromide with potassium sulphide. It is a crystalline compound, melting at  $110^{\circ}$ , and boiling at  $200^{\circ}$ . The vapor density indicates that it has the double formula,  $(C_2H_4)_2S_2$ , hence it corresponds to diethylene oxide. With bromine it yields  $C_2H_4SBr_2$ , which forms the *oxide*  $C_2H_4SO$ , when acted upon with silver oxide. Nitric acid converts the sulphide into the *sulphone*,  $C_2H_4SO_2$  (p. 110); both are crystalline compounds.

As ethylene glycol is a dihydric, di-primary alcohol, it can yield two aldehydes:—

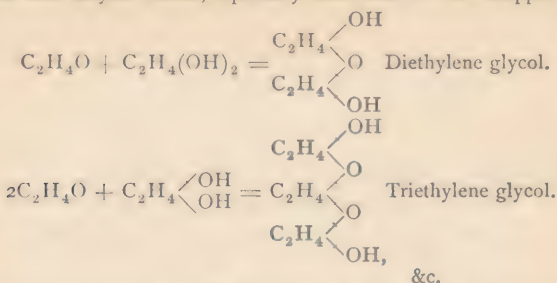


**Glycolyl Aldehyde**,  $C_2H_4O_2$ , is both an alcohol and an aldehyde. It is obtained from dichlorethyl ether,  $CH_2Cl.CHCl.O.C_2H_5$  (p. 108), when it is heated with water, or from  $CH_2(OH).CHCl.O.C_2H_5$  (from dichlor-ether), by the action of sulphuric acid. It is only known in aqueous solution. Silver oxide converts it into glycollic acid,  $CH_2(OH).CO.OH$ . *Glyoxal*,  $C_2H_2O_2$ , will receive mention under glyoxylic acid.

#### *Polyethylene Glycols or Alcohols.*

The glycols, like the other dihydroxyl compounds (see Inorganic Chemistry), can condense to polyglycols by the coalescence of several molecules, water sepa-

rating at the same time. These condensed forms arise by the direct union of the glycols with alkylen oxides, especially when heat of  $100^{\circ}$  is applied:—



The polyglycols are thick liquids, with high boiling points. They behave like the glycols. Anhydro-acids may be obtained from them by oxidation with dilute nitric acid; thus diglycollic acid (see this) is formed from diethylene alcohol.

**Diethylene Glycol**,  $(\text{C}_2\text{H}_4)_2\text{O}(\text{OH})_2$ , boils at  $250^{\circ}$ . **Triethylene Glycol**,  $(\text{C}_2\text{H}_4)_3\text{O}_2(\text{OH})_2$ , boils at  $285\text{--}290^{\circ}$ . **Tetraethylene Glycol** boils above  $300^{\circ}$ .

#### *Ethidene or Ethylidene Compounds.*

**Ethidene Oxide**,  $\text{CH}_3\text{.CH.O}$ , is ordinary acetaldehyde. On mixing with water heat is evolved, and we may suppose that, perhaps at the time, ethidene dihydrate,  $\text{CH}_3\text{.CH}(\text{OH})_2$ , is produced (p. 149).

**Ethidene-dimethyl Ether**,  $\text{CH}_3\text{.CH} \begin{array}{c} \diagup \text{O.C}_2\text{H}_5 \\ \diagdown \text{O.C}_2\text{H}_5 \end{array}$ , occurs in crude wood-spirit, and is produced in the oxidation of a mixture of methyl and ethyl alcohols; also upon heating acetaldehyde with methyl alcohol (p. 151). An ethereal liquid, boiling at  $64^{\circ}$ ; its specific gravity, equals 0.867 at  $1^{\circ}$ .

**Ethidene-methyl-ethyl Ether**,  $\text{CH}_3\text{.CH} \begin{array}{c} \diagup \text{O.C}_2\text{H}_5 \\ \diagdown \text{O.C}_2\text{H}_5 \end{array}$ , is produced together with the dimethyl ether in the oxidation of wood-spirit and alcohol. It boils at  $85^{\circ}$ .

**Ethidene-diethyl Ether**,  $\text{CH}_3\text{.CH} \begin{array}{c} \diagup \text{O.C}_2\text{H}_5 \\ \diagdown \text{O.C}_2\text{H}_5 \end{array}$ , **Acetal**, occurs in the course of the distillation of crude spirit and is produced:—

1. By oxidizing alcohol with  $\text{MnO}_2$  and sulphuric acid.
2. By heating alcohol and acetaldehyde to  $100^{\circ}$ .
3. By the action of sodium ethylate upon ethidene bromide and monochlor-ether.

Acetal is difficultly soluble in water, has an odor somewhat like that of alcohol, and boils at  $104^{\circ}$ ; at  $20^{\circ}$  its specific gravity equals 0.8314. It is rather stable in presence of alkalis; dilute acids, however, easily convert it into aldehyde and alcohol (*Berichte*, 16, 512). Chlorine produces substitution products: mono-, di-, and tri-chloroacetal,  $\text{CCl}_3\text{.CH}(\text{O.C}_2\text{H}_5)_2$ . Sulphuric acid breaks these up into alcohol and aldehyde (p. 155).

*Acid esters* of ethidene may be prepared by heating ethidene chloride with salts of the fatty acids, and by the union of aldehyde with acids, acid chlorides, and acid anhydrides (p. 151). Boiling alkalis convert them into acids and aldehydes, which are further resinified.

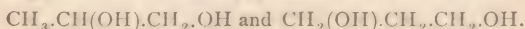
**Ethidene Chloracetate**,  $\text{CH}_3\text{.CH} \begin{array}{c} \diagup \text{O.C}_2\text{H}_5\text{O} \\ \diagdown \text{Cl} \end{array}$ , chlorinated acetic ethyl ester, boils at  $120^{\circ}$ , and is gradually decomposed by water into aldehyde, acetic acid and  $\text{HCl}$ .

**Ethidene Diacetate**,  $\text{CH}_3\cdot\text{CH} \begin{smallmatrix} \diagup \text{O.C}_2\text{H}_3\text{O} \\ \diagdown \text{O.C}_2\text{H}_3\text{O} \end{smallmatrix}$ , is not very soluble in water, boils at  $169^\circ$ , and is split into aldehyde and acetic acid when boiled with water.

Other ethidene compounds are aldehyde-ammonia,  $\text{CH}_3\cdot\text{CH} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{OH} \end{smallmatrix}$ , and aldehyde-hydrocyanide,  $\text{CH}_3\cdot\text{CH} \begin{smallmatrix} \diagup \text{CN} \\ \diagdown \text{OH} \end{smallmatrix}$  (p. 151).

## 2. Propylene Glycols, $\text{C}_3\text{H}_8\text{O}_2 = \text{C}_3\text{H}_6(\text{OH})_2$ .

The two glycols theoretically possible are known:—



$\alpha$ -Propylene Glycol

$\beta$ -Propylene Glycol.

**$\alpha$ -Propylene Glycol** is obtained by heating propylene bromide with silver acetate and saponifying the acetic ester at first produced with caustic potash. Propylene chloride, heated with water and lead oxide, also yields it. It is most readily prepared by distilling glycerol with sodium hydrate (*Berichte*, 13, 1805). It is a thick liquid, with sweetish taste. It boils at  $188^\circ$ . At  $0^\circ$  its specific gravity equals 1.051. Platinum black oxidizes it to ordinary lactic acid. Only acetic acid is formed when chromic acid is the oxidizing agent. Concentrated hydriodic acid changes it to isopropyl alcohol and its iodide.

When exposed to the action of the ferment *Bacterium termo*, ordinary propylene glycol becomes optically active and affords an active propylene oxide (*Berichte*, 14, 843).

**Propylene Diacetate**,  $\text{C}_3\text{H}_6(\text{O.C}_2\text{H}_3\text{O})_2$ , boils at  $186^\circ$ ; specific gravity 1.109 at  $0^\circ$ . The  *$\alpha$ -chlorhydrin*,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , is produced when sulphuric acid and water act upon allyl chloride. It boils at  $127^\circ$  and is oxidized to mono-chloracetic acid by nitric acid.  *$\beta$ -Chlorhydrin*,  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{OH}$ , is produced by adding  $\text{ClOH}$  to propylene. This also boils at  $127^\circ$ , but on oxidation yields  *$\alpha$ -chlorpropionic acid*,  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CO}\cdot\text{OH}$ .  *$\alpha$ -Propylene oxide*,  $\text{CH}_3\cdot\text{CH} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{CH}_2 \end{smallmatrix}$ , from the chlorhydrins, boils at  $35^\circ$ , is readily soluble in water, and yields isopropyl alcohol,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , with nascent hydrogen.

**$\beta$ -Propylene Glycol**,  $\text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2(\text{OH})$ , trimethylene glycol, is formed by boiling trimethylene bromide with a large quantity of water or potassium carbonate (*Berichte*, 16, 393). Its formation from glycerol in the *schizomycetes-fermentation* is worthy of note. It is a thick liquid, miscible with water and alcohol, boiling at  $216^\circ$ , and having a specific gravity at  $0^\circ$  of 1.065. Hydrobromic acid changes it to bromhydrin, which yields  $\gamma$ -oxybutyric acid with potassium cyanide. Moderately oxidized it affords  $\beta$ -oxypropionic acid.

Its *diacetate*,  $\text{CH}_2(\text{CH}_2\cdot\text{O.C}_2\text{H}_3\text{O})_2$ , boils at  $210^\circ$ ; its specific gravity at  $19^\circ$  is 1.07. The chlorhydrin,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , is obtained by conducting  $\text{HCl}$  into glycol. It boils at  $160^\circ$ , and its specific gravity at  $0^\circ$  is 1.146. It is soluble in

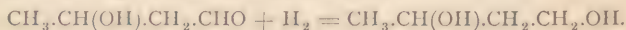
2 volumes of water, and, when oxidized with chromic acid, becomes  $\beta$ -chlorpropionic acid. *Trimethylene oxide*,  $\text{CH}_2 \begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{smallmatrix} \text{O}$ , is prepared by heating chlorhydrin with caustic potash. A mobile liquid, with penetrating odor, and boiling at  $50^\circ$ . It mixes readily with water and condenses easily.

### 3. Butylene Glycols, $\text{C}_4\text{H}_{10}\text{O}_2 = \text{C}_4\text{H}_8(\text{OH})_2$ .

Of the six possible butylene glycols (p. 253) four are known.

(1)  **$\alpha$ -Butylene Glycol**,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , is obtained from  $\alpha$ -butylene bromide; boils at  $191$ – $192^\circ$ , and at  $0^\circ$  has a specific gravity of 1.0189. Nitric acid oxidizes it to glycollic and glyoxylic acids.

(2)  **$\beta$ -Butylene Glycol**,  $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , is formed in slight quantity, together with ethyl alcohol, in the action of sodium amalgam upon aqueous acetaldehyde (p. 155). Aldol (see below) very probably appears as an intermediate product in this reaction, and from it the glycol can be directly made by the use of sodium amalgam (*Berichte*, 16, 2505):—



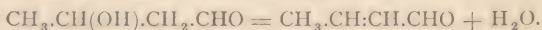
This is a thick liquid, which boils at  $207^\circ$ , and mixes with both water and alcohol. When it is oxidized by either nitric or chromic acid we get acetic and oxalic acids (along with some crotonaldehyde).

The aldehyde of this glycol is **Aldol**,  $\text{C}_4\text{H}_8\text{O}_2 = \text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHO}$ ,  $\beta$ -oxybutyraldehyde. This is obtained by letting dilute hydrochloric acid act upon crotonaldehyde (p. 159) and acetaldehyde:—



A mixture of acetaldehyde and dilute hydrochloric acid, prepared in the cold, is permitted to stand 2–3 days, at a medium temperature, until it has acquired a yellow color. It is then neutralized with sodium carbonate, shaken with ether, the latter evaporated, and the residual aldol distilled in a vacuum (*Berichte*, 14, 2069).

Aldol is a colorless, odorless liquid, with a specific gravity of 1.120 at  $0^\circ$ , and is miscible with water. Upon standing it changes to a sticky mass, which cannot be poured. Aldol distils in a vacuum undecomposed at  $100^\circ$ ; but under atmospheric pressure it loses water and becomes crotonaldehyde:—



As an aldehyde it will reduce an ammoniacal silver nitrate solution. Heated with silver oxide and water it yields  $\beta$ -oxybutyric acid,  $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

On standing it polymerizes into *paraldol*,  $(\text{C}_4\text{H}_8\text{O}_2)_n$ , which melts at  $80$ – $90^\circ$ . Should the mixture of aldehyde and hydrochloric acid used for the preparation of aldol stand for some time, water separates, and we obtain the so-called *dialdan*,  $\text{C}_8\text{H}_{14}\text{O}_3$ . This melts at  $139^\circ$ , and reduces ammoniacal silver solutions.



Ammonia converts aldol in ethereal solution into aldol-ammonia,  $C_4H_8O_2 \cdot NH_3$ , a thick syrup, soluble in water. When heated with ammonia we get the bases,  $C_8H_{15}NO_2$ ,  $C_8H_{13}NO$  (oxytetraldin, p. 159) and  $C_8H_{11}N$  (collidine). With aniline aldol forms methyl quinoline.

(3)  $\gamma$ -Butylene Glycol,  $CH_3 \cdot CH(OH) \cdot CH(OH) \cdot CH_3$ , is formed from  $\beta$  butylene bromide. It boils at  $183-184^\circ$ . Its specific gravity at  $0^\circ$  equals 1.048. Nitric acid oxidizes it to oxalic acid.

(4) Isobutylene Glycol,  $(CH_3)_2C(OH) \cdot CH_2 \cdot OH$ , is obtained from isobutylene bromide. It boils at  $176-178^\circ$ . At  $0^\circ$  its specific gravity is 1.0129. Nitric acid converts it into  $\alpha$ -oxyisobutyric acid.

Its chlorhydrin,  $(CH_3)_2CCl \cdot CH_2 \cdot OH$ , is produced by adding  $ClOH$  to isobutylene. It boils at  $128-130^\circ$ , and when oxidized becomes chlor-isobutyric acid.

4. Amylene Glycols,  $C_5H_{12}O_2 = C_5H_{10}(OH)_2$ .

(1)  $\beta$ -Amylene Glycol,  $CH_3 \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CH_3$  is derived from  $\beta$ -amylen bromide (p. 59). It boils at  $187^\circ$ . Its specific gravity at  $0^\circ$  is 0.994. By oxidation it yields  $\alpha$ -oxybutyric acid and acetic acid.

(2)  $\alpha$ -Isoamylen Glycol,  $(CH_3)_2C(OH) \cdot CH(OH) \cdot CH_3$ , from  $\alpha$  isoamylen bromide, boils at  $206^\circ$ . Its specific gravity at  $0^\circ$  is 0.998. When oxidized it affords oxy-isovaleric acid.

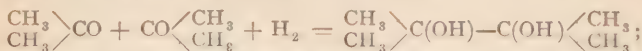
(3)  $\beta$ -Isoamylen Glycol,  $(CH_3)_2C(OH) \cdot CH(OH) \cdot CH_3$ , from  $\beta$ -isoamylen bromide, boils at  $177^\circ$ . Its specific gravity at  $0^\circ$  is 0.967. When oxidized it yields  $\alpha$ -oxy-isobutyric acid.

5. Hexylene Glycols,  $C_6H_{14}O_2$ .

(1) Hexylene Glycol,  $C_6H_{12}(OH)_2$ , from hexylene bromide, boils at  $207^\circ$ . Its specific gravity at  $0^\circ$  is 0.967.

(2) Diallyl Hydrate,  $C_6H_{12}(OH)_2$ , is obtained from diallyl,  $(C_3H_5)_2$  (p. 63), by means of the HI-compound,  $C_6H_{12}I_2$ . It boils at  $212-215^\circ$ .

3. Tetramethyl-ethylene Glycol,  $(CH_3)_2C(OH) \cdot C(OH) \cdot (CH_3)_2$ , or Pinacone, is formed, together with isopropyl alcohol, when sodium amalgam or sodium acts upon aqueous acetone (p. 161):—



it can be obtained, too, from the bromide of tetramethyl-ethylene (from dimethyl-isopropyl-carbinol). It crystallizes from its aqueous solution in the form of the hydrate,  $C_6H_{14}O_2 + 6H_2O$ , which consists of large quadratic plates, melting at  $42^\circ$ , and gradually efflorescing on exposure. In the anhydrous state it is a crystalline mass which melts at  $38^\circ$  and boils at  $171-172^\circ$ .

When heated with dilute sulphuric or hydrochloric acid pinacone parts with 1 molecule of water, and by molecular transposition, becomes *pinacoline*,  $C_6H_{12}O$  (p. 167).

Dimethyl-pinacone is the representative of a series of similarly constituted glycols—the *pinacones*. These contain two hydroxyl groups attached to two adjoining carbon atoms, which in turn are linked to two alkyls. All the pinacones exhibit similar deportment, in that when they are heated with acids they give up water and suffer molecular transposition into ketones—the *pinacolines* (p. 161)—see also benzpinacone.

Another pinacone of the fatty series is—

Methyl-ethyl Pinacone,  $\begin{array}{c} CH_3 \\ \diagup \\ C_2H_5 \end{array} > C(OH) \cdot C(OH) < \begin{array}{c} CH_3 \\ \diagdown \\ C_2H_5 \end{array}$ . This is obtained from  $\begin{array}{c} CH_3 \\ \diagup \\ C_2H_5 \end{array} > CO$ . It is a crystalline mass, melting at  $28^\circ$ , and boiling at  $200-$

205°. It does not form a hydrate with water. When heated with sulphuric acid (diluted with 1 part water) it yields pinacoline by a transposition of the methyl group :—



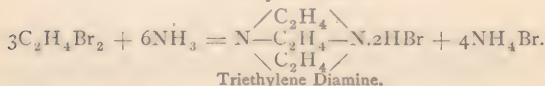
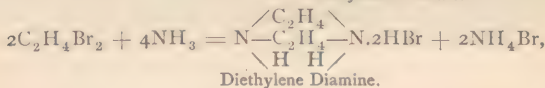
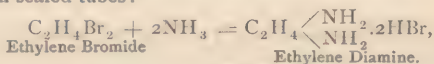
This is a liquid with an odor like that of camphor, and boils at 145–150°. When oxidized with chromic acid it decomposes into acetic acid and dimethylethyl

acetic acid,  $(\text{CH}_3)_2\text{C}(\text{C}_2\text{H}_5)\text{CO}_2\text{H}$ .

The higher glycols have been but little studied.

## AMINES OF THE DIVALENT RADICALS.

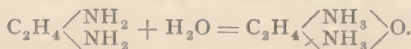
The di-, like the mono-valent alkyls, can replace two hydrogen atoms in two ammonia molecules and produce primary, secondary, and tertiary *diamines*. The latter are prepared by heating the alkylene bromides with alcoholic ammonia to 100° (p. 123) in sealed tubes :—



To liberate the diamines, the mixture of the HBr salts is distilled with KOH and the product then fractionated. Being derivatives of two ammonia molecules the diamines are di-acidic bases, capable of directly forming salts with two equivalents of the acids.

In the primary and secondary diamines the amid-hydrogen (by action of alkyl iodides) can be further substituted by alkyls, whereas the tertiary diamines unite with the alkyl iodides to ammonium iodides.

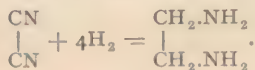
Further, the diamines unite directly with water, forming *ammonium oxides* :—



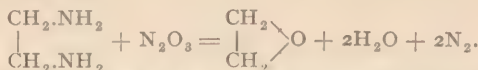
These compounds are very stable\* and only give up water when distilled over KOH. With acids they part with water and yield diamine salts.

Of the many diamine derivatives formed by these methods, we may cite the following :—

**Ethylene Diamine**,  $\text{C}_2\text{H}_4 \begin{array}{c} \diagup \text{NH}_2 \\ \diagdown \text{NH}_2 \end{array}$ , is a colorless liquid, boiling at 123°. It reacts strongly alkaline, and has an ammoniacal odor. It forms also when nascent hydrogen (tin and HCl) acts upon dicyanogen (p. 124) :—

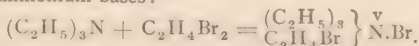


Nitrous acid converts it into ethylene oxide, ethylene glycol being very probably first formed (p. 125):—



**Di-ethylene Diamine**,  $\begin{array}{c} \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_4 \end{array} \} \text{N}_2\text{H}_2$ , boils at  $172^\circ$ . **Triethylene Diamine**,  $(\text{C}_2\text{H}_4)_3\text{N}_2$ , boils at  $210^\circ$ .

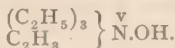
By permitting the tertiary monamines to act upon ethylene bromide we obtain the bromides of ammonium bases:—



The bromine attached to the nitrogen of these compounds can be readily replaced, whereas, the other bromine atom is more stably combined. Silver nitrate produces the nitrate of triethyl-bromethyl-ammonium:—

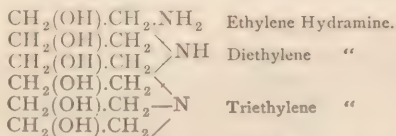


And by the action of moist silver oxide, the bromine atom in union with carbon is also attacked, HBr separates out, and the group,  $\text{CH}_2\text{Br.CH}_2$ , is changed to the vinyl group,  $\text{CH}_2:\text{CH}$ . In this manner we get the *triethyl-vinyl-ammonium base*



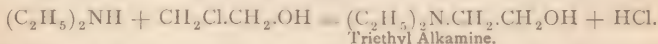
## OXYETHYL BASES OR HYDRAMINES.

When ethylene oxide and aqueous ammonia act upon each other, there occurs a direct union of 1, 2 and 3 molecules of ethylene oxide with 1 molecule of ammonia, and we obtain the bases:—



The HCl salts of these bases are produced by the action of ethylene chlorhydrin,  $\text{CH}_2\text{Cl.CH}_2.\text{OH}$ , upon ammonia. The bases are separated by fractional crystallization of their HCl-salts or platinum double salts. They are thick, strongly alkaline liquids, which decompose upon distillation.

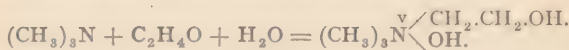
The alkylen oxides and their chlorhydrins also combine with the amines. Such oxyalkyl bases may be obtained from the allyl amines by addition of water (by the action of  $\text{H}_2\text{SO}_4$  (*Ber.*, 16, 532). The bases obtained from the secondary amines are *alkamines* or *alkines* (*Ber.*, 15, 1143):—



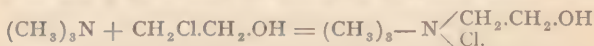
When heated with organic acids and hydrochloric acid, these oxyethyl bases form (by replacement of the hydrogen of OH by acid radicals) ester like compounds, termed *Alkēines* (see *Tropeine*).

Especially interesting are the bases obtained from the tertiary amines. Choline is one of them. It is quite important physiologically.

**Choline**,  $C_5H_{15}NO_2 = C_2H_4 \begin{smallmatrix} \diagup OH \\ \diagdown N(CH_3)_3 \end{smallmatrix} .OH$ , oxyethyl-trimethyl ammonium hydroxide. This was first discovered in the bile (hence called choline or bilineurine). It is quite widely distributed in the animal organism, especially in the brain, and in the yolk of egg, in which it is present as *lecithin*, a compound of choline with glycerophosphoric acid and fatty acids. It is obtained, too, from sinapin (the alkaloid of *Sinapis alba*), when it is boiled with alkalis (hence the name *sincalin*). Choline is artificially prepared by heating trimethyl-amine with ethylene oxide in aqueous solution:—



The HCl-salt is produced by means of ethylene chlorhydrin:—



Choline deliquesces in the air and crystallizes with difficulty. It possesses a strong alkaline reaction and absorbs  $CO_2$ . Its platinum double salt,  $(C_5H_{14}ONCl)_2 \cdot PtCl_4$ , crystallizes in beautiful reddish-yellow plates, insoluble in alcohol.

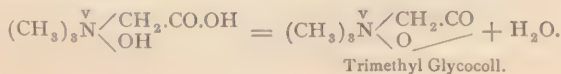
**Isocholine**,  $CH_3 \cdot CH(OH) \cdot N(CH_3)_3 \cdot OH$ , isomeric with choline, is obtained by introducing  $CH_3$  into aldehyde-ammonia (*Ber.*, 16, 207). *Muscarine*,  $C_2H_3(OH)_2 \cdot N(CH_3)_3 \cdot OH$ , is oxy-choline. It is found in fly agaric, and is formed by oxidizing choline with  $HNO_3$ .

When choline is heated with hydriodic acid, we obtain the compound,  $(CH_3)_3N \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \cdot I \\ \diagdown I \end{smallmatrix}$ . This moist silver oxide converts into *vinyl-trimethyl-ammonium hydroxide*:—



This base resembles choline; it has also been obtained from the brain substance, and bears the name **Neurine**. It is very poisonous, and is very similar to the **Ptomaines** (substances resulting from the decay of albuminoid matter), and perhaps identical with them. When choline decomposes it yields *neurine* (*Ber.*, 17, 1137).

**Betaine** (oxyneurine, lycine),  $C_5H_{11}NO_2$ , is allied to choline. It must be considered as trimethyl glycocoll (see this). It is obtained by the careful oxidation of choline, when the primary alcohol group,  $CH_2 \cdot OH$ , is converted into  $CO \cdot OH$ , and the ammonium hydroxide that is first formed parts with a molecule of water (see **Amido-acids**):—





The HCl salt is obtained directly by synthesis, when trimethylamine is heated with monochloroacetic acid :—

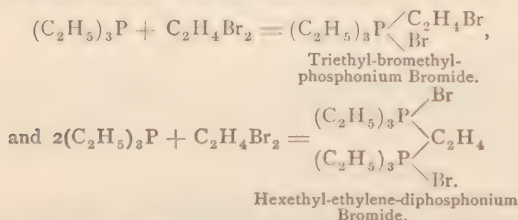


Betaïne occurs already formed in the sugar-beet (*Beta vulgaris*), hence, is present in the molasses from the beet. It crystallizes from alcohol with 1 molecule  $\text{H}_2\text{O}$  in shining crystals, which deliquesce in the air, has an alkaline reaction and a sweetish taste. At  $100^\circ$  it loses one molecule of water. When boiled with alkalis it decomposes, setting trimethylamine free.

### PHOSPHORUS BASES.

Phosphine affords a number of diphosphines, perfectly analogous to the diamines (p. 131).

When triethylphosphine acts upon ethylene bromide we obtain :—



By the action of silver nitrate or oxide upon these the phosphonium bases are set free.

Triethyl arsine,  $\text{As}(\text{C}_2\text{H}_5)_3$ , forms similar derivatives with ethylene bromide.

### SULPHONIC ACIDS OF THE DIVALENT RADICALS (p. 119).

**Methene Disulphonic Acid**,  $\text{CH}_2 \begin{array}{l} \diagup \text{SO}_3\text{H} \\ \diagdown \text{SO}_3\text{H} \end{array}$ . **Methionic acid**, is obtained by acting on acetamide or methyl cyanide with fuming sulphuric acid. The acid consists of long, deliquescent needles. The *barium salt*,  $\text{CH}_2(\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , forms pearly leaflets, and is difficultly soluble in water. Barium chloride precipitates it from a solution of the acid. The free acid is very stable and not decomposed when boiled with  $\text{HNO}_3$ .

**Hydroxymethene Sulphonic Acid**,  $\text{CH}_2 \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{SO}_3\text{H} \end{array}$ , is formed when  $\text{SO}_3$  acts upon methyl alcohol and the product is boiled with water. Very likely a compound is first produced in this reaction which is analogous to ethionic acid (p. 268). It crystallizes with difficulty and is very stable. The *barium salt* crystallizes in small plates without any water.

In addition to the preceding acid we obtain also oxymethene disulphonic acid,  $\text{CH}(\text{OH}) \begin{array}{l} \diagup \text{SO}_3\text{H} \\ \diagdown \text{SO}_3\text{H} \end{array}$ , and methine trisulphonic acid,  $\text{CH}(\text{SO}_3\text{H})_3$ .

**Ethylene Disulphonic Acid**,  $\text{C}_2\text{H}_4 \begin{array}{l} \diagup \text{SO}_3\text{H} \\ \diagdown \text{SO}_3\text{H} \end{array}$ , is produced by oxidizing glycol

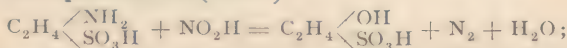
mercaptan and ethylene sulphocyanate with concentrated nitric acid; by acting upon alcohol or ether with fuming sulphuric acid; and by boiling ethylene bromide with a concentrated solution of potassium sulphite:—



The acid is a thick liquid, readily soluble in water, and crystallizes with difficulty. When it yields crystals these fuse at  $94^\circ$ . The *barium salt*,  $\text{C}_2\text{H}_4(\text{SO}_3)_2\text{Ba}$ , crystallizes from water in six-sided plates.

**Hydroxyethylene Sulphonic Acid**,  $\begin{matrix} \text{CH}_2\cdot\text{OH} \\ | \\ \text{CH}_2\cdot\text{SO}_3\text{H} \end{matrix}$ , **Isethionic**

**Acid**, oxyethylsulphonic acid,  $\text{C}_2\text{H}_4(\text{OH})\cdot\text{SO}_3\text{H}$ , is isomeric with ethyl sulphuric acid,  $\text{SO}_4\text{H}(\text{C}_2\text{H}_5)$ , and is produced by oxidizing monothioethylene glycol,  $\text{C}_2\text{H}_4\begin{matrix} \diagup \text{OH} \\ \diagdown \text{SH} \end{matrix}$ , with  $\text{HNO}_3$ ; by the action of nitrous acid upon taurine (below):—



by heating ethylene chlorhydrin with potassium sulphite:—



and further by boiling ethionic acid (p. 268) with water.

*Preparation*.—Conduct the vapors of  $\text{SO}_3$  into strongly cooled, anhydrous alcohol or ether, dilute with water and then boil for several hours. The fluid will contain isethionic, sulphuric, and some methionic acid. It is next saturated with barium carbonate and the barium sulphate removed by filtration. When the solution is evaporated methionate of barium crystallizes out first, and after further concentration barium isethionate (*Ber.*, 14, 64, and *Ann.*, 223, 198).

Isethionic acid is obtained as a thick liquid, which crystallizes to a solid when allowed to stand over sulphuric acid. Being a sulphonic acid, it is not decomposed when boiled with water. Its salts are very stable and crystallize well.

The *barium salt* is anhydrous. The *ammonium salt* forms rhombic plates, which fuse at  $135^\circ$ , and at  $210$ – $220^\circ$  it changes to di-isethionic acid (*Ber.*, 14, 65). *Ethyl isethionate*,  $\text{C}_2\text{H}_4(\text{OH})\cdot\text{SO}_3\cdot\text{C}_2\text{H}_5$ , boils at  $120^\circ$ , and appears to form in the distillation of the diethyl sulphuric ester (p. 116), see *Ber.*, 15, 947. Chromic acid oxidizes the isethionic acid to sulpho-acetic acid.

$\text{PCl}_5$  converts the acid or its salts into the *chloride*,  $\text{C}_2\text{H}_4\begin{matrix} \diagup \text{Cl} \\ \diagdown \text{SO}_2\cdot\text{Cl} \end{matrix}$ , a liquid, boiling at  $200^\circ$ . When it is boiled with water it is converted into chlorethylsulphonic acid,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$  (*Ann.*, 223, 212).

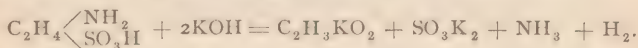
**Taurine**,  $\text{C}_2\text{H}_7\text{NSO}_3$ , Amido-ethylsulphonic acid,  $\text{C}_2\text{H}_4\begin{matrix} \diagup \text{NH}_2 \\ \diagdown \text{SO}_3\text{H} \end{matrix}$ , occurs as taurocholic acid in combination with cholic acid in the bile of oxen and many other animals, and also in the different animal secretions. It may be artificially prepared by heating chlor-

ethylsulphonic acid,  $\text{CH}_2\text{Cl}.\text{CH}_2.\text{SO}_3\text{H}$  (from isethionic acid with  $\text{PCl}_5$ ), with aqueous ammonia.

Taurine crystallizes in large, monoclinic prisms, insoluble in alcohol, but readily dissolved by hot water. It melts and decomposes at about  $240^\circ$ .

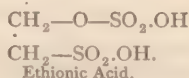
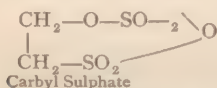
Taurine contains the groups  $\text{NH}_2$  and  $\text{SO}_3\text{H}$ , and is, therefore, both a base and a sulphonic acid. But as the two groups neutralize each other the compound has a neutral reaction. It can, however, form salts with the alkalis. It separates unaltered from its solution in acids (see Glycocoll).

Nitrous acid converts it into isethionic acid (p. 267). Boiling alkalis and acids do not affect it, but when fused with caustic potash it breaks up according to the equation:—



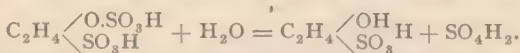
By introducing methyl into taurine we obtain tauro-betaïne, analogous to betaïne (p. 265):  $(\text{CH}_3)_3\text{N} \begin{smallmatrix} \text{C}_2\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{SO}_2.$

When the vapors of  $\text{SO}_3$  are passed through anhydrous alcohol the so-called *Carbyl Sulphate*,  $\text{C}_2\text{H}_4\text{S}_2\text{O}_6$  (*Ann.*, 223, 210), results. We can regard this as the anhydride of ethionic acid:—

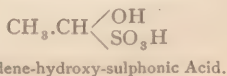
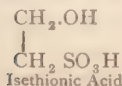
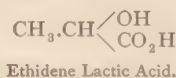
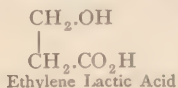


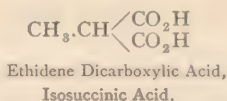
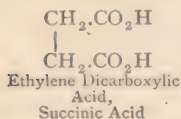
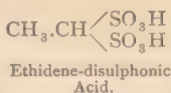
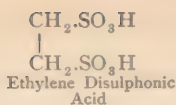
Carbyl sulphate also arises in the direct union of ethylene with 2 molecules of  $\text{SO}_3$ . It is a deliquescent, crystalline mass, fusing at  $80^\circ$ . With water it yields:

**Ethionic Acid**,  $\text{C}_2\text{H}_4 \begin{smallmatrix} \text{O}.\text{SO}_3\text{H} \\ \diagup \\ \text{SO}_3\text{H} \end{smallmatrix}$ . Its constitution would indicate it to be both a sulphonic acid and primary sulphuric ester. It is therefore dibasic, and on boiling with water readily yields sulphuric and isethionic acids:—



*Ethidene Sulphonic Acids.* The following grouping is intended to express the relations of the sulphonic acids of this group with those of ethylene and the corresponding carboxylic acids:—





The compounds formed by the union of aldehydes with alkaline sulphites (p. 151), are viewed as salts of ethidene-hydroxy-sulphonic acid :—



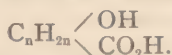
The *potassium salt* is anhydrous and forms needles; the *sodium salt*,  $\text{C}_2\text{H}_4(\text{OH}).\text{SO}_3\text{Na} + \text{H}_2\text{O}$ , consists of shining leaflets. When these are heated with water they decompose into aldehyde, water and sulphites.

*Ethidene chlorsulphonic Acid*,  $\text{CH}_3.\text{CH} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{SO}_3\text{H} \end{array}$ , *α-chlorethyl sulphonic acid*, is obtained by heating ethidene chloride with aqueous neutral sodium sulphite to  $140^\circ$ . The acid is tolerably stable and yields salts which crystallize well. The *sodium salt* forms pearly leaflets.

*Ethidene Disulphonic Acid*,  $\text{CH}_3.\text{CH}(\text{SO}_3\text{H})_2$ , results when thioaldehyde or thialdine is oxidized with  $\text{MnO}_4\text{K}$ . It affords very stable salts (*Ber.*, 12, 682).

## DIVALENT MONOBASIC ACIDS.

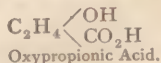
### OXY-FATTY ACIDS.



Acids of this series, with the empirical formula,  $\text{C}_n\text{H}_{2n}\text{O}_3$ , show a twofold character in their entire deportment. Since they contain a carboxylic group, they are *monobasic acids* with all the attaching properties and transpositions of the latter; the OH group linked to the radical bestows upon them all the properties of the *monohydric alcohols*. They may, therefore, be designated as *alcohol acids* (corresponding to the ketonic acids. p. 214). They were formerly called *divalent or dihydric (diatomic) acids*, as they contained two hydroxyl groups (an alcoholic and an acidic) and could be obtained by oxidizing the dihydric alcohols (p. 256). At present they are mostly termed *oxy- or hydroxy-fatty acids*, because of their origin from the fatty-acids by the replacement of an hydrogen atom by OH :—



and

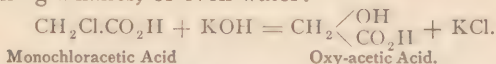


This view of them is especially well adapted for the nomenclature of the acids (p. 272).



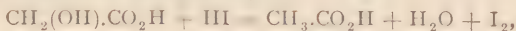
The following are the chief methods of producing the oxy-acids:—

1. By the transposition of the mono-halogen fatty acids with silver oxide, boiling alkalies, or even water:—

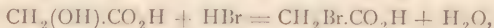


The conditions of the reaction are perfectly similar to those observed in the conversion of the alkyl halogens into alcohols (p. 89). The  $\alpha$ -derivatives yield  $\alpha$ -oxy-acids; the  $\beta$ -derivatives are occasionally changed to unsaturated acids by the splitting-off of an haloid acid (p. 179), while the  $\gamma$ -compounds afford  $\gamma$ -oxy-acids, which subsequently pass into lactones.  $\gamma$ -Halogen acids are converted directly into lactones by the alkaline carbonates.

The oxy-acids can be reconverted into fatty acids by heating them with hydriodic acid (p. 67):—

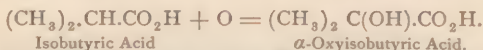


or are first changed to monobrom-acids with hydrobromic acid:—



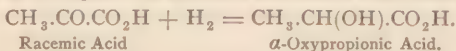
and the product reduced with nascent hydrogen.

2. Some fatty acids have OH directly introduced into them. This is accomplished by oxidizing them with  $\text{KMnO}_4$  in alkaline solution:—

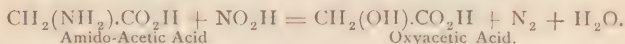


Only acids containing the tertiary group  $\text{CHI}$  (a so-called tertiary H-atom) are adapted to this kind of transposition (*Annalen*, 208, 60, 220, 56). Nitric acid effects the same as  $\text{MnO}_4\text{K}$  (*Berichte*, 14, 1782, 15, 2318).

3. The action of nascent hydrogen (sodium amalgam, zinc and hydrochloric acid) upon the ketonic acids and their esters (p. 214):—

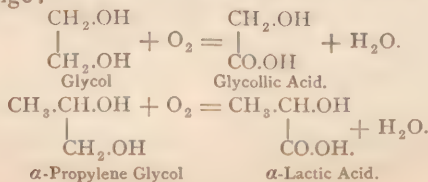


4. By the action of nitrous acid upon amido-acids:—

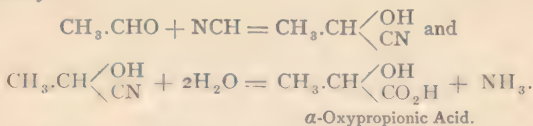


This reaction is perfectly similar to that observed in the conversion of amines into alcohols (p. 125).

5. Careful oxidation of the glycols with dilute nitric acid or platinum sponge:—



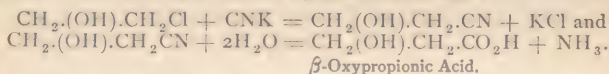
6. By letting hydrocyanic acid and hydrochloric acid act upon the aldehydes and ketones. At first oxycyanides are produced (p. 151), after which hydrochloric acid changes the cyanogen group into carboxyl:—



*α*-Oxypropionic Acid.

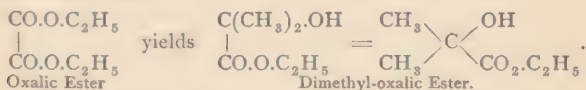
In preparing the oxycyanides the aldehydes or ketones are heated under pressure with the equivalent amount of hydrocyanic acid (from 20–30 per cent). Or we can add pulverized potassium cyanide to the ethereal solution of the ketone, and follow it with the gradual addition of concentrated hydrochloric acid (*Berichte*, 14, 1965, 15, 2318). The concentrated hydrochloric acid changes the cyanides to acids, the amides of the acids being at first formed in the cold, but on boiling with more dilute acids they sustain further change to acids. Sometimes the change occurs more readily by heating with a little dilute sulphuric acid.

The glycol chlorhydrins (p. 255) undergo a like alteration through the action of potassium cyanide and acids:—



*β*-Oxypropionic Acid.

7. A method of ready applicability in the synthesis of oxyacids consists in permitting zinc and alkyl iodides to act upon diethyl oxalic ester (Frankland and Duppa). This reaction is like that in the formation of tertiary alcohols from the acid chlorides by means of zinc ethyl, or of the secondary alcohols from formic esters (p. 190)—1 and 2 alkyl groups are introduced into one carboxyl group (*Annalen*, 185, 184).



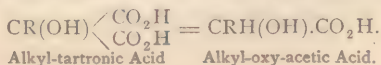
Oxalic Ester

Dimethyl-oxalic Ester.

If we employ two alkyl iodides two different alkyls may be introduced.

The acids obtained, as indicated, are named in accordance with their derivation from oxalic acid, but it would be more correct to view them as derivatives of oxy-acetic acid or glycollic acid,  $\text{CH}_2(\text{OH}) \cdot \text{CO}_2\text{H}$ , and designate, *e. g.*, dimethyl-oxalic acid as dimethyl-oxyacetic acid.

8. The fatty acids are formed from alkyl malonic acids,  $\text{CRR}'(\text{CO}_2\text{H})_2$ , by withdrawal of one carboxyl group (p. 169), and the oxy-fatty acids are obtained in a similar manner from alkyl oxymalonic acids or tartronic acids:—



Alkyl-tartronic Acid

Alkyl-oxy-acetic Acid.

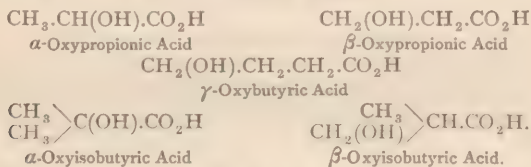
The tartronic compounds are synthetically prepared from malonic acid esters, *e. g.*,  $\text{CH}_2 \begin{smallmatrix} \diagup \text{CO}_2 \cdot \text{C}_2\text{H}_5 \\ \diagdown \text{CO}_2 \cdot \text{C}_2\text{H}_5 \end{smallmatrix}$ , by first introducing the alkyl group (see Malonic acid), then replacing the second hydrogen of  $\text{CH}_2$  by chlorine, and finally saponifying the alkylic monochlor-malonic ester with baryta (*Ber.*, 14, 619). The successive transformations correspond to the formulas:—



The possible isomerides of the divalent acids are best derived from their corresponding monobasic acids, by replacing an hydrogen atom in the latter by OH.

Only one oxy-acid can be derived from acetic acid, viz., glycollic acid,  $\text{CH}_2\text{OH} \cdot \text{COOH}$ . From propionic acid,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , we can obtain two oxy-acids. Five isomerides agree with the formula,  $\text{C}_4\text{H}_8\text{O}_3 = \text{C}_3\text{H}_6 \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$ ; three of them are derived from normal butyric acid,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , and two from isobutyric acid,  $(\text{CH}_3)_2\text{CH} \cdot \text{CO}_2\text{H}$ , etc.

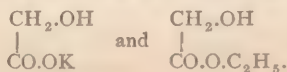
The above compounds are named like the substituted fatty acids (p. 179), *i. e.*, as  $\alpha$ -,  $\beta$ -,  $\gamma$ -, etc., oxy-acids:—



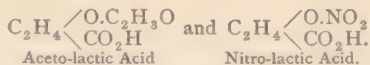
The  $\alpha$ - and  $\beta$ -oxy-acids exist free, whereas the  $\gamma$ -acids are only known in their salts and acids. When liberated from the latter they immediately give up a molecule of water and pass into their anhydrides, the lactones. Various other peculiarities also distinguish them (p. 273).

The oxy-fatty acids containing one OH group are, in consequence, more readily soluble in water, and less soluble in ether than the parent acids (p. 254). They are, further, less volatile, and as a general thing, cannot be distilled without undergoing a change.

Their chemical properties fully accord with their structure, by which they are both acids and alcohols. The acidic hydrogen (of the carboxyl group) can be easily replaced by metals and hydrocarbon residues, thus giving rise to normal salts and esters:—

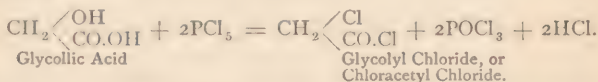


The remaining OH-group deports itself like that of the alcohols. Alkali metals and alkyls may replace its hydrogen. Acid radicals and  $\text{NO}_2$  are substituted for it by the action of chlorides of monobasic acid radicals (like  $\text{C}_2\text{H}_3\text{O.Cl}$ ), and a mixture of concentrated nitric and sulphuric acids:—



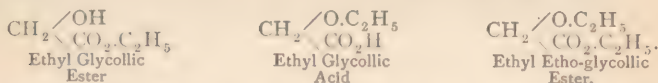
Both of these reactions are characteristic of the hydroxyl groups of the alcohols (p. 257).

$\text{PCl}_5$  replaces both OH's by chlorine:—



The Cl in union with CO is very reactive with water and alcohols, yielding free acids and their esters; in the case cited, monochloroacetic acid,  $\text{CH}_2\text{Cl.CO}_2\text{H}$ , and its esters result.

The various esters of the divalent acids exhibit similar relations:—



Alkalies cause the alkyl combined with  $\text{CO}_2$  to separate, forming ethyl glycollic acid,  $\text{CH}_2 \begin{array}{l} \diagup \text{O.C}_2\text{H}_5 \\ \diagdown \text{CO}_2\text{H} \end{array}$ .

See *Ber.*, 15, 162, upon the formation of esters of the oxy-acids.

In the preceding transpositions all the oxy-acids react similarly, but in those following they exhibit variations influenced by the position of the OH group.

Their varying behavior when oxidized is characteristic, especially when chromic acid is employed as the oxidizing agent (p. 162).

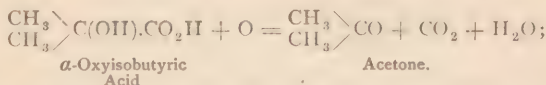
The *primary* oxy-acids, containing the primary alcohol group,  $\text{CH}_2\text{OH}$ , may have the latter converted into aldehyde, and carboxyl groups (p. 253), and the products will then be aldehyde-acids and dicarboxylic acids. Thus, from glycollic acid are derived glyoxylic and oxalic acids:—



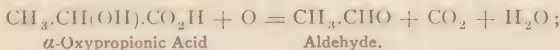
The *secondary* oxy-acids, with the secondary alcoholic group,



$>\text{CH.OH}$ , can afford ketones, which, however, pass very readily into other compounds (p. 218). The  $\alpha$ -oxy-acids, too, lose carboxyl when boiled with a chromic acid mixture. In them the  $\text{CO}_2\text{H}$  and  $\text{OH}$  groups are attached to one carbon atom. Should the latter be linked to two hydrocarbon residues, ketones and  $\text{CO}_2$  are produced:—

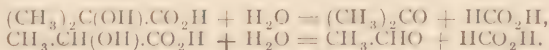


whereas, if it be in combination with only one such group, aldehydes are first formed:—



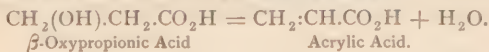
and these can then be further oxidized to acids.

The  $\alpha$ -oxyacids undergo a like decomposition when heated with dilute sulphuric or hydrochloric acid (or by action of concentrated  $\text{H}_2\text{SO}_4$ ). Their carboxyl group is removed as formic acid (when concentrated  $\text{H}_2\text{SO}_4$  is employed,  $\text{CO}$  and  $\text{H}_2\text{O}$  are the products):—

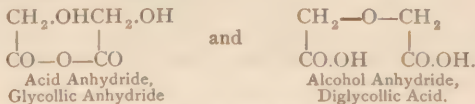


Another alteration is sustained by the  $\alpha$ -oxy-acids at the same time; it, however, does not extend far. Water is eliminated and unsaturated acids are produced. This change is easily effected when  $\text{PCl}_3$  is allowed to act on the esters of  $\alpha$ -oxy-acids (p. 190).

When the  $\beta$ -oxy-acids are heated alone or with acids, water is withdrawn and unsaturated acids are almost the sole products (p. 270):—

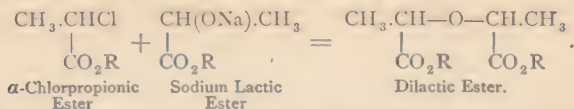


*Anhydrides of the Oxy-acids.*—The anhydrides of the oxy-acids may be produced in three ways. If two molecules of the acids unite so that the water can be withdrawn from the carboxyl groups, the true or real acid anhydrides are formed. These are perfectly analogous to the anhydrides of the fatty acids (p. 200). If the water should arise from the alcohol hydroxyls, then the products are *alcohol anhydrides* or *anhydridic acids*:—



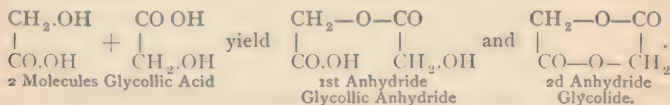
The acid anhydrides of the oxy-fatty-acids have not yet been prepared. The alcohol anhydrides, like diglycollic acid, correspond perfectly to the ethers and sometimes appear on heating the oxy-acids. As a general thing they are prepared according to the same methods as the ethers of the alcohols. Thus diglycollic acid (and some glycollic acid) is obtained from monochloroacetic acid,  $\text{CH}_2\text{Cl.CO}_2\text{H}$ , by

the action of bases (lime water or lead oxide); further, dilactic acid (its esters) is made from  $\alpha$ -chloropropionic ester and sodium lactic ester:—



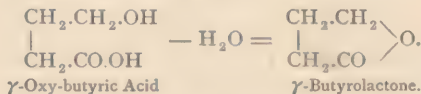
These ether-acids (anhydridic acids), like the alcohol ethers, break up into oxy-acids on heating them with hydrochloric acid to  $100^\circ$ .

In the *third* class of anhydrides, the *ester anhydrides*, the reaction is between the OH's of carboxyl and the alcohol (p. 203). Should *two* molecules of the oxy-acid react we may have the single and double ester formation. Glycollic acid affords a first and second ester anhydride:—



From lactic acid ( $\alpha$ -oxy-propionic acid),  $\text{C}_3\text{H}_6\text{O}_3$ , we get lactic anhydride,  $\text{C}_6\text{H}_{10}\text{O}_5$ , and the so-called *Lactide*,  $\text{C}_6\text{H}_8\text{O}_4$  (p. 283). Only the  $\alpha$ -oxy-acids are capable of affording this simple and double “ester anhydride formation” by the union of two molecules. Heat hastens the reaction (occurs on standing in the dessicator). Conversely the ester anhydrides when heated with water absorb it and oxy-acids are regenerated.

Should the anhydride formation occur with one and the same molecule of the oxy-acids, we get what are designated *lactones* (*Fittig, Ann., 208, 111; 216, 27*):—

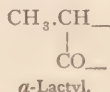


The  $\gamma$ - and  $\delta$ -oxy-acids (from mono- and dicarboxylic acids) especially are adapted to this lactone formation, hence we distinguish  $\gamma$ - and  $\delta$ -lactones (*Ann., 216, 127*). In the first we have a chain of four, in the second a chain of five carbon atoms closed by oxygen. This resembles the union in the anhydrides of the dibasic acids. Generally the lactones are liquids, easily soluble in water, alcohol, and ether. They show neutral reaction, possess a faintly aromatic odor, and can be distilled without decomposition. The alkaline carbonates precipitate them from their aqueous solution in the form of oils. The  $\gamma$ -lactones are characterized by great stability. They are partially converted into oxy-acids by water, but this only occurs after protracted boiling, whereas those of the  $\delta$ -variety gradually absorb water at the ordinary temperature and soon react acid (*Ber., 16, 373*). Boiling alkaline carbonates convert lactones into oxy-acid salts. The caustic alkalis effect this more readily. If the oxy-acids are freed from their salts by the

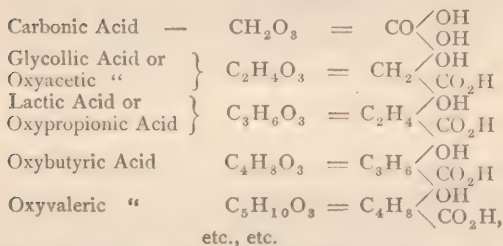
mineral acids they at once break up into water and lactones. Heat hastens the conversion. Lactones combine with halogen hydrides and ammonia to yield halogen and amido-fatty acids. These regenerate the lactones readily (*Ber.*, 17, 201). They are obtained from the corresponding monohalogen fatty-acids upon boiling the latter with alkalis, and supersaturating with mineral acids. Alkaline carbonates immediately throw out the lactones. They may be formed also from unsaturated acids by heating with hydrobromic acid or sulphuric acid (diluted with 1 volume  $H_2O$ ) (*Ber.*, 16, 373). See Isocaprolactone.

Besides the  $\gamma$ - and  $\delta$ -oxy-acids, some of the  $\beta$ -oxy-acids (of the benzene class) are capable of yielding corresponding lactones ( $\beta$ -lactones) (*Ber.*, 16, 3001; 17, 415). The latter are far less stable, passing readily into oxy-acids and splitting off carbon dioxide. It appears almost certain that an  $\alpha$ -lactone also exists (*Ber.*, 15, 579).

The divalent groups, attached to the two OH's in the oxy-acids, are often called radicals :—



### OXY-ACIDS $C_nH_{2n}O_3$ .



1. **Carbonic Acid**,  $CH_2O_3$ —oxyformic acid—is the lowest member of the series. It cannot exist free, and its character varies considerably from those of the rest. From its symmetrical structure and the fact that no difference exists in the OH groups, this compound is a *dibasic* acid, although very feeble. Therefore it and its numerous derivatives will be treated later, after the other divalent acids.

2. **Glycollic Acid**,  $C_2H_4O_3 = CH_2(OH).CO_2H$ .

Glycollic, or oxyacetic acid, is obtained according to the methods given as follows: from ethylene glycol, from monochlor- or brom-acetic acid, and from amido-acetic acid,  $CH_2(NH_2)$ .

$\text{CO}_2\text{H}$ , by means of nitrous acid. It is produced, also, when nascent hydrogen acts upon oxalic acid :—



by oxidizing ethyl alcohol with nitric acid at ordinary temperatures (with glyoxal and glyoxylic acid, p. 278); from glycosin and its derivatives, and from glycerol by the action of silver oxide (*Ber.* 16, 2414).

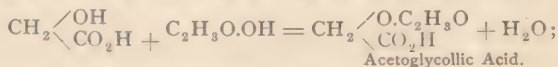
The best method of preparing the acid is to boil chloracetic acid with alkalis or calcium carbonate. The calcium salt first formed is decomposed with an equivalent amount of oxalic acid and the filtrate concentrated (*Ber.*, 16, 2954.)

Glycollic acid is a thick syrup, which gradually crystallizes upon standing over sulphuric acid. The crystals melt at  $80^\circ$  and deliquesce in the air. It dissolves easily in water, alcohol and ether. When distilled it decomposes with formation of trioxymethylene (p. 153).

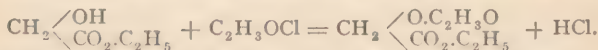
Its alkali salts are very deliquescent. The *calcium salt*,  $(\text{C}_2\text{H}_3\text{O}_3)_2\text{Ca}$ , with 3 and 4  $\text{H}_2\text{O}$ , is difficultly soluble in cold water (1 part in 8 parts  $\text{H}_2\text{O}$  at  $10^\circ$ ), and crystallizes in needles. The *silver salt*,  $(\text{C}_2\text{H}_3\text{O}_3\text{Ag})_2 + \text{H}_2\text{O}$ , is also rather insoluble. The *ethyl ester*,  $\text{CH}_2(\text{OH}).\text{CO}_2.\text{C}_2\text{H}_5$ , is a liquid, possessing a specific gravity equal to 1.03 and boils at  $150^\circ$ .

Alcohol and acid radicals can replace the hydrogen in alcohol-hydroxyl of glycollic acid. The *acid derivatives* are formed :—

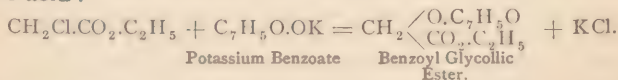
(1) On heating glycollic acid with monobasic acids :—



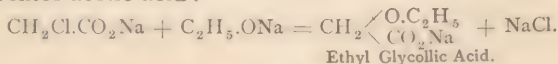
or by acting upon esters of the acid with acid chlorides :—



(2) By action of the alkali salts of acids upon esters of monochlor-acetic acid :—



We obtain the *alcohol derivatives* when sodium alcoholates act on monochlor-acetic acid :—



**Methyl Glycollic Acid**,  $\text{CH}_2 \begin{array}{l} \diagup \text{O.CH}_3 \\ \diagdown \text{CO}_2\text{H} \end{array}$ , boils at  $198^\circ$ ; **ethyl glycollic acid**,  $\text{CH}_2(\text{O.C}_2\text{H}_5).\text{CO}_2\text{H}$ , at  $206^\circ$ . Both are very stable, and boiling alkalis do not decompose them.



The *ether-esters*, like  $\text{CH}_2 \begin{smallmatrix} \diagup \text{O} \cdot \text{CH}_3 \\ \diagdown \text{CO}_2 \cdot \text{CH}_3 \end{smallmatrix}$ , result when chloracetic esters are acted upon by sodium alcoholates. For their boiling points see *Ber.*, 17, 486.

**Thioglycollic Acid**,  $\text{CH}_2 \begin{smallmatrix} \diagup \text{SH} \\ \diagdown \text{CO}_2 \text{H} \end{smallmatrix}$ , is both an acid and a mercaptan. It is obtained from monochloracetic acid and potassium sulphhydrate; from thiohydantoïn (see this), and its phenyl derivatives, when they are heated with alkalis (*Annalen*, 207, 124). It is an oil, which is readily soluble in water, alcohol and ether. Heat decomposes it. On adding ferric chloride to the acid solution, then neutralizing with ammonia, we obtain a purple-red coloration. Thioglycollic acid behaves like a dibasic acid, forming primary and secondary salts, *e. g.*,  $\text{CH}_2(\text{SAg})\text{CO}_2\text{Ag}$ . This is due to the SH group imparting the properties of the mercaptans.

**Nitrosothioglycollic Acid**,  $\text{CH} \begin{pmatrix} \text{SH} \\ \text{NO} \end{pmatrix} \cdot \text{CO}_2\text{H}$ , is crystalline. Ferric chloride colors it blue.

#### Anhydrides of Glycollic Acid.

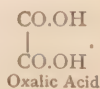
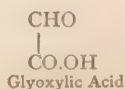
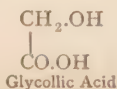
**Glycollic Anhydride**,  $\text{C}_4\text{H}_6\text{O}_5 = \text{CH}_2(\text{OH})\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , the first ester anhydride of glycollic acid (p. 275), is produced on heating glycollic acid to  $100^\circ$ . It is a solid, insoluble in alcohol, water and ether. It melts at  $128\text{--}130^\circ$ . Boiling water changes it to glycollic acid.

**Glycolide**,  $\text{C}_4\text{H}_4\text{O}_4 = \begin{smallmatrix} \text{CH}_2\text{---O---CO} \\ \text{CO---O---CH}_2 \end{smallmatrix}$ —the second ester anhydride of glycollic acid (p. 275)—is obtained by strongly igniting glycollic acid (to  $250^\circ$ ) or tartronic acid, and by heating potassium or silver glycollate (*Berichte*, 14, 577). It forms a powder almost insoluble in water, and melts at  $220^\circ$ . It returns to glycollic acid when boiled with water. When heated with ammonia it yields glycolamide,  $\text{CH}_2 \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$ , which boils at  $120^\circ$ . Formerly glycolide was sup-

posed to be an ester anhydride (p. 275) with the formula,  $\text{CH}_2 \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{CO} \end{smallmatrix}$ . The present double formula is assigned it from its analogy to lactide (p. 283).

**Diglycollic Acid**,  $\text{C}_4\text{H}_6\text{O}_5$ , the alcohol anhydride of glycollic acid (p. 274), is formed on boiling monochloracetic acid with lime, baryta,  $\text{MgO}$  or  $\text{PbO}$  (also with glycollic acid), and in the oxidation of diethylene glycol,  $\text{O} \begin{smallmatrix} \diagup \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \end{smallmatrix}$  (p. 259), with nitric acid and platinum sponge. The acid crystallizes in rhombic prisms, which melt at  $148^\circ$ . Boiling alkalis do not alter it. It is only when heated with concentrated hydrochloric acid to  $120^\circ$  that it breaks up into glycollic acid. The acid is dibasic, yielding primary and secondary salts. The calcium salt is difficultly soluble.

**Glyoxal and Glyoxylic Acid** are intimately related to glycollic acid and glycol:—



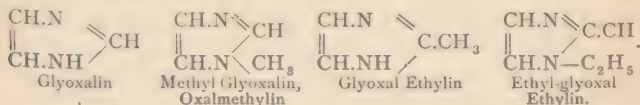
Glyoxal is the dialdehyde of ethylene glycol, while the so-called glycolyl aldehyde (p. 258) represents the first or half aldehyde. Glyoxylic acid is the aldehyde of glycollic acid, and may also be termed the half aldehyde of oxalic acid. Glyoxal, glycollic acid and glyoxylic acid are formed in the careful oxidation of ethylene glycol, ethyl alcohol, or acetaldehyde with nitric acid. Further oxidation converts them into oxalic acid.

In preparing glyoxal, alcohol, or better, aldehyde and fuming nitric acid are placed, layer after layer, in narrow glass cylinders, using a funnel tube for the introduction of the acid. Let the whole stand for 5-6 days (*Berichte*, 14, 2685). The residue obtained by evaporation of the mixture to syrup consistence contains chiefly glyoxal, with a little glycollic acid and glyoxylic acid. These can be removed in the form of calcium salts. To obtain the glyoxal, the residue is directly treated with a concentrated solution of primary sodium sulphite, when the double salt with glyoxal (see below) will crystallize out (*Berichte*, 17, 169).

**Glyoxal**,  $C_2H_2O_2 = CHO.CHO$ , a dialdehyde. It forms a white amorphous mass, which deliquesces in the air, and dissolves readily in alcohol and ether. When oxidized it yields glyoxylic and oxalic acids. Alkalies convert it, even in the cold, into glycollic acid,  $CH_2(OH).CO_2H$ . As a dialdehyde it unites directly with 2 molecules of primary sodium sulphite, forming the crystalline compound,  $C_2H_2O_2(SO_3HNa)_2$ . It also reduces ammoniacal silver solutions. On warming a dilute solution of it with potassium cyanide, it acquires a dark-red color.

With ammonium cyanide and hydrochloric acid, glyoxal forms diamido-succinic acid (p. 151). It also yields a dioximid-compound with two molecules of hydroxylamine; this is the so-called **Glyoxim**,  $CH(N.OH).CH(N.OH)$  (p. 164). It is soluble in water, alcohol and ether. It crystallizes in rhombic plates, melts at  $178^\circ$ , and sublimes without difficulty. It has a faintly acid reaction, and forms salts with the bases.

Concentrated ammonia yields two bases with glyoxal: **Glycosin**,  $C_6H_6N_4$ , and in larger quantity, **Glyoxalin**,  $C_3H_4N_2$ . The latter affords a series of derivatives bearing the names *glyoxalins* or *oxalins*. The following formulas express their constitution:—



They would thus be closely allied to the amidines (p. 249), and the anhydro-bases and lophines of the benzene series. Like all these amidines, they do not afford acetyl compounds with acid chlorides (*Ber.*, 16, 285, 545, 748). When the glyoxalins are acted upon with hydrogen peroxide, they become oxamides (*Ber.*, 17, 1289).

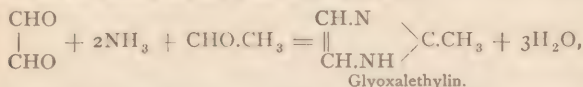
**Glyoxalin**,  $C_3H_4N_2$ , from glyoxal and ammonia (*Ber.*, 10, 1365, 15, 645) is easily soluble in water, alcohol and ether. It crystallizes in brilliant prisms, melting at  $89^\circ$ , and boiling at  $255^\circ$ . It reacts strongly alkaline, affords crystalline salts with 1 equivalent of the acids, and is an imide base. Alkyl iodides and caus-

tic potash cause a substitution of alkyl for the imide hydrogen, forming *alkyl glyoxalins* (*Ann*, **214**, 319). These are liquids, which boil without decomposition, have a peculiar odor, and unite with alkyl iodides to produce ammonium iodides.

**Methyl Glyoxalin**,  $C_3H_3N_2.CH_3$ , boils at  $199^\circ$ , and is identical with the so-called oxalmethylin, obtained from dimethyl oxamide (see this).

**Propyl Glyoxalin**,  $C_3H_3N_2.C_3H_7$ , boils near  $221^\circ$ .

The glyoxalethylin (homologues of glyoxalin, see above), are isomeric with these alkyl glyoxalins. They are obtained by letting ammonia act upon a mixture of glyoxal and an aldehyde (*Ber.*, **15**, 2706, **16**, 487) :—



or of glyoxal upon aldehyde ammonia (*Ber.*, **16**, 487). The glyoxalethylin are crystalline solids, in deportment like glyoxalin, and resemble the alkaloids. They are mon-acidic imide bases, with the imide hydrogen replaced by alkyls, just as in glyoxalin.

**Glyoxalethylin**,  $C_3H_2(CH_3)N_2H$ , crystallizes in brilliant needles, which melt at  $137^\circ$ , and boil at  $267^\circ$ . It is identical with **Paraoxalmethylin**, which is produced from methyl-glyoxalin,  $C_3H_3N_2CH_3$  (by molecular transposition), when the latter is distilled with lime. It may also be obtained from ethyl glyoxalethylin,  $C_3H_2(CH_3)N_2.C_2H_5$  (by the splitting-off of ethylene)—(*Ber.*, **14**, 424).

When methyl is introduced into glyoxalethylin, we get :—

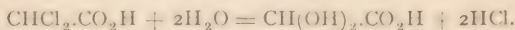
**Methyl Glyoxalethylin**,  $C_3H_2(CH_3)N_2.CH_3$ , which boils at  $205^\circ$ . **Ethyl glyoxalethylin**,  $C_3H_2(CH_3)N_2.C_2H_5$ , boils at  $212^\circ$ . It is identical with **oxalethylin**, obtained from diethyl oxamide,  $C_2O_2(NH.C_2H_5)_2$ , (see this).

**Glyoxalpropylin**,  $C_3H_2(C_2H_5)N_2H = C_2H_2 \begin{array}{c} \diagup N \\ \diagdown NH \end{array} \text{C}.CH_2.CH_3$ , melts at  $89^\circ$ , and boils at  $268^\circ$ . It is identical with **oxalpropylin** (*Ber.*, **16**, 490).



glyoxylic acid. The aldehydes frequently yield hydrates by combining with 1 molecule of  $H_2O$ ; these derivatives are regarded as dihydroxyl compounds (see chloral hydrate, p. 156). Glyoxylic acid exhibits similar behavior. The free crystalline acid has the formula,  $C_2H_3O_3.H_2O = C_2H_4O_4$ ; all its salts are obtained from it. Hence, we must consider it a dihydroxyl compound, which may be designated a dioxy-acetic acid. By withdrawal of water, the aldehyde group is produced, and the acid conducts itself as a true aldehyde acid.

Glyoxylic acid is obtained by oxidizing glycol, alcohol and aldehyde (p. 279). It is most readily prepared by heating dichlor- and dibrom-acetic acid to  $120^\circ$  with water :—



It is a thick liquid, readily soluble in water, and crystallizes in rhombic prisms by long standing over sulphuric acid. The crystals

possess the formula  $C_2H_4O_4$ . It distils undecomposed with steam. As a monobasic acid it affords salts with 1 equivalent of acid. When dried at  $100^\circ$ , the salts have the formula,  $C_2H_3MeO_4$ . The ammonium salt alone has the formula,  $C_2H(NH_4)O_3$ . The calcium salt,  $(C_2H_3O_4)_2Ca$ , crystallizes with 1 and 2 molecules  $H_2O$  (*Ber.* 14, 585), and is difficultly soluble in water (in 140 parts at  $18^\circ$ ). Lime water precipitates an insoluble basic salt from its solution. The silver salt,  $C_2H_3AgO_4$ , is a white, crystalline precipitate.

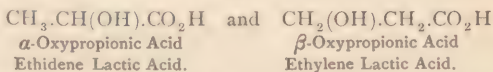
Again, glyoxylic acid manifests all the properties of an aldehyde. It reduces ammoniacal silver solutions with formation of a mirror, and combines with primary alkali sulphites. When oxidized (silver oxide), it yields oxalic acid; by reduction (zinc and water) it forms glycollic acid:  $CHO.CO_2H + H_2 = CH_2(OH).CO_2H$ . On boiling the acid or its salts with lime water or alkalies glycollic and oxalic acids are produced (*Ber.*, 13, 1392):—



This is analogous to the transposition of aldehydes to alcohol and acid (p. 150). When  $CNH$  and  $HCl$  act upon glycollic acid, a like transposition ensues.

### 3. Lactic Acids or Oxypropionic Acids, $C_3H_6O_3$ .

There are two possible isomerides:—



(1) **Ethidene Lactic Acid, Ordinary Lactic Acid of Fermentation**,  $CH_3.CH(OH).CO_2H$ , is formed by a peculiar fermentation of sugar (milk sugar, cane sugar), gum and starch, in the presence of albuminoid substances (chiefly casein). It is, therefore, contained in many substances which have soured, *e. g.*, in sour-milk, in sour-kraut, pickles, also in the gastric juice. The lactic fermentation occurs by the action of a particular, organized ferment, at temperatures from  $35$ – $45^\circ$ . Excess of free acid arrests it, but it is renewed, if the acid be neutralized by alkalies.

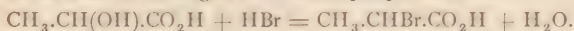
The acid is artificially prepared by the methods already described, p. 270: from  $\alpha$ -chlor- or brom-propionic acid by boiling with alkalies; from  $\alpha$ -propylene glycol by oxidation with nitric acid; from alanine,  $CH_3.CH(NH_2).CO_2H$ , by means of nitrous acid, and by the action of nascent hydrogen upon racemic acid. Other methods are to heat grape sugar and cane sugar with water and 2–3 parts barium hydrate, to  $160^\circ$ , and  $\alpha$ -dichloroacetone,  $CH_3.CO.CHCl_2$ , with  $H_2O$  to  $200^\circ$ .



Lactic acid is usually obtained by the fermentation of cane sugar. 3 Kilo-grams cane sugar and 15 grams tartaric acid are dissolved in 17 litres of water, and the solution let stand several days. Then add 100 grams decaying cheese, previously macerated in 4 litres of sour-milk, and 1200 grams zinc-white, and let the mixture ferment at 40–45° for 8–10 days (longer fermentation changes the lactic into butyric acid). The entire mass is next brought to boiling, filtered, and the filtrate strongly concentrated. The zinc lactate which separates out is decomposed by  $\text{H}_2\text{S}$ , the  $\text{ZnS}$  removed by filtration, and the filtrate containing the lactic acid evaporated on the water bath. To separate the lactic acid produced in this manner from the mannitol (formed simultaneously) dissolved by it, shake the residue with ether, which will not dissolve the mannitol.

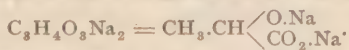
Fermentation lactic acid is a thick syrup, with a specific gravity 1.215, but it cannot be obtained crystallized. It is miscible with water, alcohol and ether, and absorbs moisture when exposed to the air. Placed in a dessicator over sulphuric acid it partially decomposes into water and the anhydride. When distilled it yields lactide, aldehyde, carbon monoxide and water.

Heated to 130° with dilute sulphuric acid it decomposes into aldehyde and formic acid (p. 274); when oxidized with chromic acid acetic acid and carbon dioxide are formed. Heated with hydrochloric acid it changes to  $\alpha$ -bromopropionic acid:—



Hydriodic acid at once reduces it to propionic acid.

The sodium salt is an amorphous mass. When heated with metallic sodium, the alcoholic hydrogen is replaced, and we get the *disodium compound*:—

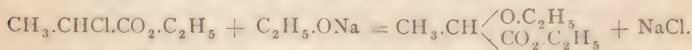


The *calcium salt*,  $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Ca} + 5\text{H}_2\text{O}$ , crystallizes in hard warts, consisting of concentrically grouped needles. It is soluble in ten parts cold water, and is very readily dissolved by hot water and alcohol.

The *zinc salt*,  $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Zn} + 3\text{H}_2\text{O}$ , crystallizes in shining needles, which dissolve in 58 parts cold and 6 parts hot water. The *iron salt*,  $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Fe} + 3\text{H}_2\text{O}$ , is very difficultly soluble in water, and yields crusts consisting of delicate needles. It is also obtained by boiling whey with iron filings. The salts of *lactic acid* are called lactates.

*Ethyl Lactic Ester*,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$ , is formed when lactic acid and anhydrous alcohol are heated to 170°. It is a neutral liquid, which boils at 156°. It is soluble in water, and rapidly decomposes into lactic acid and alcohol. When potassium and sodium act upon the ester, they replace alcoholic hydrogen, and if the product be treated with ethyl iodide we obtain:—

*Ethyl Etholactic Ester*,  $\text{CH}_3\cdot\text{CH} \begin{array}{l} \text{O.C}_2\text{H}_5 \\ \diagdown \\ \text{CO}_2\cdot\text{C}_2\text{H}_5 \end{array}$ . This is formed also on heating  $\alpha$ -chlorpropionic ester (or lactyl chloride) with sodium ethylate:—



It boils at 156°, and is insoluble in water. When the ester is boiled with caustic soda ethyl-lactic acid is produced.

*Ethyl Lactic Acid*,  $\text{CH}_3\cdot\text{CH}\begin{smallmatrix} \diagup \text{O.C}_2\text{H}_5 \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$ . A strongly acid syrup, yielding crystalline salts, which reafford the diethyl ester when acted upon with ethyl iodide. Hydriodic acid breaks it up into lactic acid and ethyl iodide:—



On adding lactic acid to a mixture of nitric and sulphuric acids (p. 257) it dissolves, forming *nitrolactic acid*,  $\text{CH}_3\cdot\text{CH}\begin{smallmatrix} \diagup \text{O.NO}_2 \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$ . A yellow liquid, little soluble in water. It decomposes readily. Its specific gravity equals 1.35.

**Lactyl Chloride**,  $\text{CH}_3\cdot\text{CH}\begin{smallmatrix} \diagup \text{Cl} \\ \diagdown \text{CO.Cl} \end{smallmatrix}$ ,  $\alpha$ -chlorpropionyl chloride, is obtained by the distillation of dry lime lactate (1 part) with  $\text{PCl}_5$  (2 parts). It is separated imperfectly from the  $\text{PCl}_3\text{O}$  which is formed at the same time. With water it affords  $\alpha$ -chlorpropionic acid; with alcohol  $\alpha$ -chlorpropionic ester. Lactic acid is regenerated when the chloride is heated with alkalis.

#### ANHYDRIDES OF LACTIC ACID.

**Lactic Anhydride**,  $\text{C}_6\text{H}_{10}\text{O}_5$ , the first ester anhydride of lactic acid (p. 275). It is formed when lactic acid is heated to  $130^\circ$ , or when it stands over sulphuric acid; further, by the action of potassium lactate upon  $\alpha$ -brompropionic acid:—



It is an amorphous powder, almost insoluble in water. The alkalis immediately convert it into lactic acid.

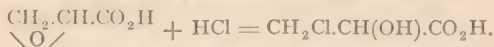
**Lactide**,  $\text{C}_6\text{H}_8\text{O}_4 = \text{CH}_3\cdot\text{CH-O-CO} \begin{smallmatrix} \diagup \text{CO-O-CH.CH}_3 \\ \diagdown \end{smallmatrix}$ , the second ester anhydride, is obtained by distilling lactic acid, or by passing dry air through the acid heated to  $150^\circ$ . It crystallizes from alcohol in rhombic plates, melting at  $124.5^\circ$  and boiling at  $255^\circ$ . It dissolves slowly in water with gradual formation of lactic acid. The vapor density agrees with the formula,  $\text{C}_6\text{H}_8\text{O}_4$  (*Ber.*, 7, 755). It was formerly believed that it was "an inner anhydride,"  $\text{CH}_3\cdot\text{CH}\begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{O} \end{smallmatrix}$ .

**Dilactic Acid**,  $\text{C}_6\text{H}_{10}\text{O}_5 = \text{CH}_3\text{—CH—O—CH.CH}_3 \begin{smallmatrix} | \text{CO}_2\text{H} \quad \text{CO}_2\text{H} \end{smallmatrix}$ . The diethyl ester is produced on heating  $\alpha$ -brompropionic ester with sodium lactic ester (p. 275) in alcoholic solution. It boils at  $235^\circ$ , and when heated above  $100^\circ$  with water, breaks up into lactic acid and alcohol.

#### SUBSTITUTED LACTIC ACIDS.

**$\beta$ -Chlorlactic Acid**,  $\text{CH}_2\text{Cl.CH(OH).CO}_2\text{H} = \text{C}_3\text{H}_5\text{ClO}_3$ , is formed by the oxidation of epichlorhydrin and  $\alpha$ -chlorhydrin,  $\text{CH}_2\text{Cl.CH(OH).CH}_2\text{.OH}$ , with concentrated  $\text{HNO}_3$ ; by the addition of hypochlorous acid to acrylic acid (together with  $\alpha$ -chlorhydracrylic acid (p. 286):

$\text{CH}_2\text{:CH.CO}_2\text{H}$  yields  $\text{CH}_2\text{Cl.CH(OH).CO}_2\text{H}$  and  $\text{CH}_2\text{(OH).CHCl.CO}_2\text{H}$ ;  
 Acrylic Acid  $\beta$ -Chlorlactic Acid  $\alpha$ -Chlorhydracrylic Acid.  
 and by the addition of  $\text{HCl}$  to epihydrinic acid (glycidic acid):—



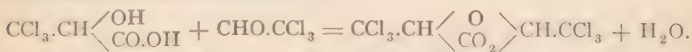
Brom- and iod- acetic acids are obtained in the same manner (*Ber.*, 14, 937). The first melts at  $89^\circ$ – $90^\circ$ , the second at  $100^\circ$ – $101^\circ$ .  $\beta$ -Chlorlactic acid is also formed from monochloraldehyde by the action of  $\text{CNH}$  and hydrochloric acid (p. 271).

$\beta$ -Chlorlactic acid crystallizes from water in large transparent plates or prisms, and melts at  $78^\circ$ – $79^\circ$ . Silver oxide converts it into glyceric acid; when reduced with hydriodic acid it becomes  $\beta$ -iodpropionic acid. Heated with alcoholic potash it is again changed to epihydrinic acid (see above), just as ethylene oxide is obtained from glycolchlorhydrin (p. 255).

Dichlorlactic Acid,  $\text{CHCl}_2\text{.CH(OH).CO}_2\text{H}$ , is obtained from dichloraldehyde through the cyanide (p. 271). It forms deliquescent plates, melting at  $77^\circ$ . It reduces ammoniacal silver solutions.

**Trichlorlactic Acid**,  $\text{CCl}_3\text{.CH(OH).CO}_2\text{H}$ , is made by heating chloralcyanhydrin,  $\text{CCl}_3\text{.CH} \begin{smallmatrix} \text{OH} \\ \diagup \quad \diagdown \\ \text{CN} \end{smallmatrix}$  (p. 151), with concentrated hydrochloric acid. It is a crystalline mass, melting at  $105^\circ$ – $110^\circ$ , and soluble in water, alcohol and ether. Alkalies easily change it to chloral, chloroform and formic acid. Zinc and hydrochloric acid reduce it to dichlor- and mono-chloracrylic acids (p. 191). Its ethyl ester melts at  $66^\circ$ – $67^\circ$  and boils at  $235^\circ$ . The best method of preparing it consists in heating chloralcyanhydrin with alcohol and sulphuric acid.

When trichlorlactic acid is heated to  $150^\circ$  with excess of chloral, we obtain *trichlorethidene-trichlorlactic ester*:—



The same body,  $\text{C}_5\text{H}_2\text{Cl}_6\text{O}_3$ , called **Chloralide**, was at first prepared by heating chloral (1 part) with fuming sulphuric acid (3 parts) to  $105^\circ$ . It crystallizes from alcohol and ether in large prisms, is insoluble in water, melts at  $114^\circ$ – $115^\circ$  and boils at  $272^\circ$ – $273^\circ$ . When heated to  $140^\circ$  with alcohol, it breaks up into trichlorlactic ester and chloral alcoholate. Chloral also unites with lactic and other oxy-acids, like glycollic, malic, salicylic, etc., forming the so-called *chloralides*.

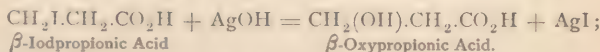
**Tribromlactic Acid**,  $\text{CBr}_3\text{.CH(OH).CO}_2\text{H}$ , from bromal cyanhydrin, melts at  $141$ – $143^\circ$  and unites with chloral and bromal to corresponding chloralides and bromalides.

**Sarco-lactic or Paralactic Acid** is a peculiar modification of fermentation lactic acid. It is present in different animal organs, especially in the juice of the flesh. Liebig's Beef Extract furnishes it. In all its transpositions it behaves like ordinary lactic acid, hence we must accept the same chemical structure for it. The existence of the two modifications is explained by the asymmetry of

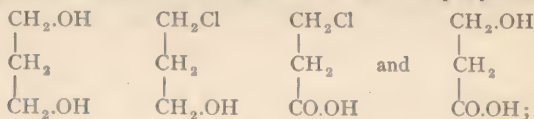
a carbon atom in the acid (p. 42). Sarco-lactic acid is distinguished from the ordinary variety by turning the plane of polarization to the right (the ordinary acid is inactive) and by differences in its salts. When heated to  $130^{\circ}$  it yields lactic anhydride (p. 283), which water changes back to ordinary lactic acid.

Its *calcium salt*,  $(C_3H_5O_3)_2Ca$ , has only  $4H_2O$  and is more difficultly soluble in water than that of ordinary lactic acid. The *zinc salt* contains  $2H_2O$ , yields shining, thick prisms and is more soluble (1 part in 17 parts  $H_2O$  at  $15^{\circ}$ ) in water than the zinc salt of ordinary lactic acid.

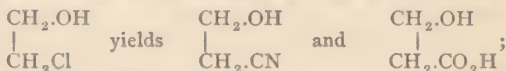
**2. Ethylene Lactic Acid, or Hydracrylic Acid,  $CH_2(OH).CH_2.CO_2H$ ,**  $\beta$ -oxypropionic acid, is obtained from  $\beta$ -iodpropionic acid on heating it with moist silver oxide or on boiling with water :—



by the careful oxidation of  $\beta$ -propylene glycol (p. 260), or by conversion of the same into chlorhydrin and  $\beta$ -chlorpropionic acid :—

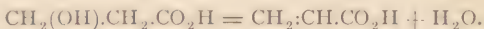


by the action of CNK and HCl upon ethylene chlorhydrin :—



and from ethylene oxide through the agency of CNH and HCl. The formation of the acid from acrylic acid by heating with aqueous sodium hydrate to  $100^{\circ}$  is also very interesting.

The free acid yields a non-crystallizable, thick syrup. When heated alone or when boiled with sulphuric acid (diluted with 1 part  $H_2O$ ) it loses  $H_2O$  and forms acrylic acid (hence the name *hydracrylic acid*, p. 274) :—



Hydriodic acid again changes it to  $\beta$ -iodpropionic acid. It yields oxalic acid and  $CO_2$  when oxidized with chromic acid or nitric acid.

The *sodium salt*  $C_3H_5O_3Na$ , is indistinctly crystalline, and melts without change at  $142\text{--}143^{\circ}$ . The *calcium salt*,  $(C_3H_5O_3)_2Ca + 2H_2O$ , forms large rhombic prisms, loses its water of crystallization at  $100^{\circ}$ , and fuses at  $140\text{--}145^{\circ}$  without decomposition. Heated to  $190^{\circ}$  it parts with water and becomes calcium acrylate. The *zinc salt*,  $(C_3H_5O_3)_2Zn + 4H_2O$ , crystallizes from a moderately concentrated solution, in large, shining prisms, and at  $150^{\circ}$  dissolves in an equal



part of water. If the solution is very concentrated it will only crystallize with difficulty. The zinc salt is soluble in alcohol, whereas the latter precipitates zinc  $\alpha$ -lactate and paralactate.

$\alpha$  Chlorhydracrylic Acid,  $\text{CH}_2(\text{OH}).\text{CHCl}.\text{CO}_2\text{H}$ , from acrylic acid, is a liquid, and is converted into hydracrylic acid by nascent hydrogen; it yields glycidic acid with the alkalis.

#### 4. Oxybutyric Acids, $\text{C}_4\text{H}_8\text{O}_3 = \text{C}_3\text{H}_6(\text{OH}).\text{CO}_2\text{H}$ .

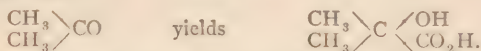
Four of the five possible oxybutyric acids are known:—

(1)  $\alpha$ -Oxybutyric Acid,  $\text{CH}_3.\text{CH}_2.\text{CH}(\text{OH}).\text{CO}_2\text{H}$ , is obtained by boiling  $\alpha$ -brombutyric acid with moist silver oxide or caustic potash, and from propionic aldehyde with  $\text{CNH}$  and  $\text{HCl}$ . It is crystalline and deliquescent in the air. It melts at  $43\text{--}44^\circ$ . The *zinc salt*,  $(\text{C}_4\text{H}_7\text{O}_3)_2\text{Zn} + 2\text{H}_2\text{O}$ , crystallizes from water in white leaflets, difficultly soluble in cold water. When oxidized with chromic acid, the acid decomposes into propionic acid and  $\text{CO}_2$ .

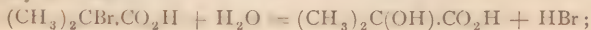
(2)  $\beta$ -Oxybutyric Acid,  $\text{CH}_3.\text{CH}(\text{OH}).\text{CO}_2\text{H}$ , is formed by the action of sodium amalgam upon aceto-acetic ester (p. 219), by the oxidation of aldol (p. 261) with silver oxide, and from  $\alpha$ -propylene chlorhydrin,  $\text{CH}_3.\text{CH}(\text{OH}).\text{CH}_2\text{Cl}$ , (p. 260) by the action of  $\text{CNK}$  and subsequent saponification of the cyanide. It is a thick, non-crystallizable syrup, which volatilizes with steam. The *Ca-* and *Zn-salts* are amorphous and readily soluble in water. When heated the acid decomposes (like all  $\beta$ -oxy-acids, p. 274) into water and crotonic acid,  $\text{CH}_3.\text{CH}:\text{CH}.\text{CO}_2\text{H}$ .

(3)  $\gamma$ -Oxybutyric Acid,  $\text{CH}_2(\text{OH}).\text{CH}_2.\text{CH}_2.\text{CO}_2\text{H}$ , is not very stable in a free condition, because it readily breaks up, like all  $\gamma$ -oxy-acids (p. 276), into water and its anhydride, **butyrolactone**,  $\text{C}_4\text{H}_6\text{O}_2$ . The acid (its salts) is obtained by letting sodium amalgam act on succinyl chloride,  $\text{C}_2\text{H}_4(\text{CO}.\text{Cl})_2$ , and from the bromhydrin of  $\beta$ -propylene glycol (p. 260) by means of  $\text{CNK}$  and the after-saponification of the cyanide, and from butyrolactone carboxylic acid (see this), by the splitting-off of  $\text{CO}_2$  (*Ber.*, 16, 2592). Butyrolactone is a neutral, thick liquid, boiling at  $203^\circ$ ; its specific gravity equals 1.130 at  $20^\circ$ .

(4)  $\alpha$ -Oxyisobutyric Acid,  $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} \text{C}(\text{OH}).\text{CO}_2\text{H}$ , was first obtained by the action of  $\text{CNH}$  and  $\text{HCl}$  on acetone (p. 162), hence called *acetonetic acid*:—



It is further obtained from oxalic ester by the action of  $\text{CH}_3\text{I}$  and  $\text{Zn}$  (see p. 271), hence termed dimethyloxalic acid, or better, dimethyl-oxyacetic acid; from  $\alpha$ -bromisobutyric acid on boiling with baryta water:—



from  $\beta$ -isoamylene glycol by oxidation with nitric acid (p. 262), (hence called butyl lactic acid); from isobutyric acid,  $C_4H_8O_2$ , by oxidizing with  $MnO_2/K$  (p. 270), and from acetone chloroform (p. 162), by aid of alkalis. Oxy-isobutyric acid crystallizes in prisms and is very soluble in water and ether. It sublimes at  $50^\circ$ , in long needles, melts at  $79^\circ$  and distils at  $212^\circ$ . Methacrylic acid is formed when  $PCl_3$  acts on its esters, (p. 193). When oxidized with chromic acid, it breaks up into acetone and  $CO_2$ .

The *barium salt*,  $(C_4H_7O_3)_2Ba$ , consists of easily soluble shining needles. The *zinc salt*,  $(C_4H_7O_3)_2Zn + 2H_2O$ , crystallizes in microscopic, six-sided plates, difficultly soluble in water.

(5)  $\beta$ -Oxyisobutyric Acid,  $CH_2.OH.CH(CH_3).CO_2H$ , has not been obtained.

## 5. Oxyvaleric Acids, $C_5H_{10}O_3 = C_4H_8(OH).CO_2H$ .

$\gamma$ -Oxyvaleric Acid,  $CH_3.CH(OH).CH_2.CH_2.CO_2H$ , like all the  $\gamma$ -oxy-acids, decomposes when separated from its salts into water and its inner anhydride, *valerolactone*,  $C_5H_8O_2$  (p. 276). The latter is prepared directly from  $\gamma$ -brom-valeric acid (from allyl acetic p. 194), on heating it with  $H_2O$  above  $100^\circ$ . It may be obtained more readily by acting on  $\beta$ -aceto-propionic acid (*lævulinic acid*, p. 224), with sodium amalgam and water. Sulphuric acid is added to the solution and the latter shaken with ether. Valerolactone is a colorless liquid which does not solidify at  $-18^\circ$  and boils at  $206-207^\circ$ . It is miscible with water, forming a neutral solution from which it is reprecipitated by alkaline carbonates. When boiled with alkalis, baryta or lime it forms  $\gamma$ -oxyvalerates (*Ann.*, 208, 104).

(2)  $\alpha$ -Oxyisovaleric Acid,  $(CH_3)_2.CH.CH(OH).CO_2H$ , is obtained from  $\alpha$ -bromisovaleric acid and from isobutyraldehyde,  $(CH_3)_2CH.CHO$ , by means of  $CNH$  and  $HCl$ . It crystallizes in large rhombic plates, which melt at  $86^\circ$  and volatilize at  $100^\circ$ . Its *ethyl ester*, boiling at  $175^\circ$ , is obtained from oxalic ester by  $Zn$  and isopropyl iodide. Heated with sulphuric acid it decomposes into isobutyraldehyde and formic acid, and when oxidized with chromic acid it yields isobutyric acid and  $CO_2$ . Heated to  $200^\circ$  it affords an anhydride,  $(C_5H_8O_2)_2$  (?) (p. 275), resembling lactide. It melts at  $136^\circ$ .

(3)  $\beta$ -Oxyisovaleric Acid,  $(CH_3)_2C(OH).CH_2.CO_2H$ , is formed on oxidizing dimethyl-allylcarbinol (p. 91) with chromic acid, or isopropyl acetic acid,  $(CH_3)_2CH.CH_2.CO_2H$ , with an alkaline  $KMnO_4$  solution (p. 270). It is a liquid which is not volatile with steam. Chromic acid oxidizes it to acetone, acetic acid and carbon dioxide.

(4) Methyl-ethyl Oxyacetic Acid,  $\begin{matrix} CH_3 \\ | \\ C_2H_5 \end{matrix} > C(OH).CO_2H$ ,  $\alpha$ -methyl- $\alpha$ -oxy-butyric acid, is obtained from methyl-ethyl acetic acid (p. 184), by oxidation with a solution of potassium permanganate; from oxalic ester by means of  $CH_3I$ ,  $C_2H_5I$  and zinc; and from methyl-ethyl ketone by means of  $CNH$  and  $HCl$ . It is crystalline, melts at  $68^\circ$ , and sublimes at  $100^\circ$ . Hydriodic acid reduces it to methyl-ethyl acetic acid, while  $CrO_3$  oxidizes it to methyl-ethyl ketone and  $CO_2$ . Its *ethyl ester* boils at  $165^\circ$ .

(5)  $\alpha$ -Methyl- $\beta$ -oxybutyric Acid,  $\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} > CH.CO_2H$ , is obtained from methyl aceto-acetic ester,  $CH_3.CO.CH(CH_3).CO_2.C_2H_5$  (p. 220). It is a liquid, which decomposes when distilled or heated with  $HI$ , into water and methyl crotonic acid.

### 6. Oxycaproic Acids. $C_6H_{12}O_3 = C_5H_{10}(OH).CO_2H$ .

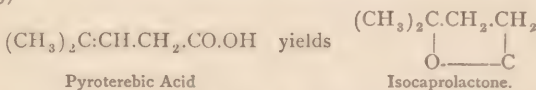
(1) *α*-Oxycaproic Acid,  $CH_3.(CH_2)_3.CH(OH).CO_2H$ , is probably the so-called leucic acid, obtained from leucine by the action of nitrous acid.

It is crystalline, melts at  $73^\circ$ , and sublimes near  $100^\circ$ . The oxycaproic acid obtained from bromcaproic acid appears to be different. This compound melts at  $60-62^\circ$  (*Ber.*, 14, 1401).

(2) *γ*-Oxycaproic Acid,  $CH_3.CH_2.CH(OH).CH_2.CH_2.CO_2H$ , like a *γ*-oxyacid, decomposes when free into  $H_2O$  and its lactone, **Caprolactone**,  $C_6H_{10}O_2$ . The latter is obtained from bromcaproic acid (from hydrosorbic acid and  $HBr$ , p. 198), on heating the latter with water (*Ann.*, 208, 67). It is a liquid, boiling at  $200^\circ$ , and dissolves in 5-6 volumes  $H_2O$  at  $0^\circ$ . On heating, caprolactone again separates. Nitric acid oxidizes it to succinic acid.

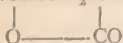
(3) *δ*-Oxycaproic Acid,  $CH_3.CH(OH).(CH_2)_3.CO_2H$ , is formed from *γ*-aceto-butyric acid (p. 225). It furnishes a *δ*-lactone (p. 275), which melts at  $18^\circ$ , and boils at  $230^\circ$ . It forms a neutral solution with water, but this becomes acid after some time.

(4) *γ*-Oxyisocaproic Acid,  $(CH_3)_2.C(OH).CH_2.CH_2.CO_2H$ . When free, this breaks up into water and the corresponding lactone, **Isocaprolactone**,  $C_6H_{10}O_2$ . The latter appears in oxidizing isocaproic acid with  $KMnO_4$  or  $HNO_3$ ; by the distillation of terebic acid (see this), and in the transposition of pyroterebic acid (p. 195), when heated alone or with hydrobromic acid (*Annalen*, 208, 55).



Isocaprolactone melts near  $7^\circ$ , boils at  $206-207^\circ$ , and is soluble in double its volume of water at  $0^\circ$ . When the solution is heated, it becomes turbid and the lactone separates. Dilute nitric acid oxidizes a  $CH_3$  group in caprolactone (also in valerolactone) to carboxyl (*Ber.*, 15, 2324).

(5) *γ*-Oxy-*α*-methylvaleric Acid,  $CH_3.CH(OH).CH_2.CH \begin{array}{l} \diagup CH_3 \\ \diagdown CO_2H \end{array}$ , and its lactone, *α*-Methylvalerolactone, or symmetrical caprolactone,  $CH_3.CH.CH_2.CH.CH_3$



, are obtained from *β*-aceto-isobutyric acid (p. 225), by action of nascent hydrogen, and by reducing saccharin,  $C_6H_{10}O_5$ , with hydriodic acid (*Ber.*, 16, 1821). The lactone boils at  $206^\circ$ , and dissolves in 20 volumes of water. Further heating with  $HI$ , changes it to methyl-propyl acetic acid (p. 185).

(6) *γ*-Oxy-*β*-methylvaleric Acid,  $CH_3.CH(OH).CH(CH_3).CH_2.CO_2H$ , and its lactone, *β*-methyl valerolactone, are obtained from *β*-aceto-butyric acid (p. 225). The lactone boils at  $210^\circ$ .

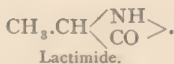
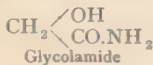
### (7) Oxyheptylic Acids, $C_7H_{14}O_3$ .

The **heptolactone**,  $C_7H_{12}O_2$ , corresponding to *γ*-oxyheptylic acid, is formed on reducing teracrylic acid,  $C_7H_{12}O_2$  (p. 195), with  $HBr$ , just as iso-caprolactone is obtained from pyroterebic acid (see above). Heptolactone melts at  $11^\circ$ , and boils at  $220^\circ$ . It dissolves in 12 volumes  $H_2O$  at  $0^\circ$ .

Many other higher oxy-fatty acids have been obtained from oxalic ester by means of propyl iodide, amyl iodide, etc., and zinc, and also from the higher aceto-acetic esters, by the use of sodium amalgam. The unsaturated acids, *allyl oxyacetic acid*,  $C_3H_5.CH(OH).CO_2H$ , and *diallyl oxyacetic acid*,  $(C_3H_5)_2C(OH).CO_2H$ , are produced in a similar manner.

## AMIDES OF THE DIVALENT ACIDS.

In the divalent acids both the alcoholic and acid hydroxyl group can be replaced by the amid-group,  $\text{NH}_2$ . In the first instance *amic* or *amido-acids* result, while in the second case we get the isomeric *acid amides* (p. 207). The *imides* result by substituting the divalent acid radicals for  $2\text{H}$ 's in ammonia (p. 276):—



## 1. Amides.

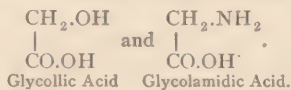
**Glycolamide**,  $\text{C}_2\text{H}_5\text{NO}_2 = \text{CH}_2 \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{CO.NH}_2 \end{array}$ , is directly produced on heating glycolide (p. 278) with dry ammonia, or from acid ammonium tartronate raised to  $150^\circ$ . It crystallizes in needles, melting at  $120^\circ$ , possesses a sweet taste, and dissolves easily in water, but with difficulty in alcohol. When boiled with alkalis it splits into glycollic acid and ammonia.

**Lactamide**,  $\text{C}_3\text{H}_7\text{NO}_2 = \text{CH}_3.\text{CH} \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{CO.NH}_2 \end{array}$ , is obtained by the union of lactide with ammonia, and upon heating ethyl lactic ester with ammonia. It forms crystals, readily soluble in water and alcohol, and melts at  $74^\circ$ . Boiling alkalis break it up into lactic acid and ammonia.

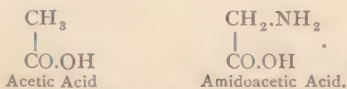
**Lactimide**,  $\text{C}_3\text{H}_5\text{NO} = \text{C}_3\text{H}_4\text{O.NH}$ , is produced by heating alanine,  $\text{CH}_3.\text{CH} \begin{array}{l} \diagup \text{NH}_2 \\ \diagdown \text{CO}_2\text{H} \end{array}$ , in a current of  $\text{HCl}$  to  $180$ – $200^\circ$ . It consists of colorless leaflets or needles, which melt at  $275^\circ$ , and dissolve readily in water and alcohol.

## 2. Amic or Amido-Acids.

Here the alcoholic hydroxyl is replaced by the group  $\text{NH}_2$ :—



It is simpler to view them as amido-derivatives of the mono-basic fatty acids, produced by the replacement of  $\text{H}$  in the latter by the amido-group:—



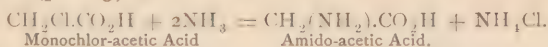
Hence they are usually called *amido-fatty acids*. The firm union of the amido-group especially distinguishes them from the isomeric acid amides. Boiling alkalis do not eliminate it (similar to the amines). Several of these amido-acids occur already formed in animal organisms. Great physiological importance attaches to them here. They have received the name *alanines* or *glycocolls* from their most important representatives.

The general methods in use for preparing the amido-acids are:—

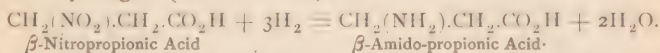
(1) The transposition of the monohalogen fatty acids when heated



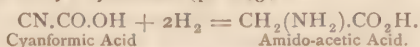
with ammonia (similar to the formation of the amines from the alkylgens (p. 123):—



(2) The reduction of nitro- and isonitroso acids (p. 171) with nascent hydrogen (Zn and HCl):—

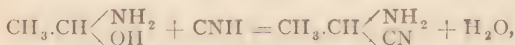


(3) Transposition of the cyan-fatty acids (p. 212) with nascent H (Zn and HCl, or by heating with HI), just as the amines are produced from the alkyl cyanides (p. 243):—



Cyanformic acid and glycolic acid are formed by the same method from dicyanogen.

(4) A synthetic method consists in heating the aldehyde-ammonias with hydrocyanic acid and hydrochloric acid (p. 151 and 271):—

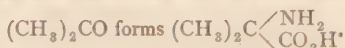


from which the amido-acids are obtained on boiling with hydrochloric acid.

A more advantageous method is to convert the cyanides of aldehydes (p. 151) into amid-cyanides by means of alcoholic ammonia (in equivalent quantity):—

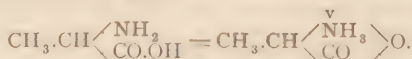


and saponify these with HCl (*Ber.*, 14, 1965)). In this manner the ketones can also be changed through the cyanides (p. 162) to amido-acids:—



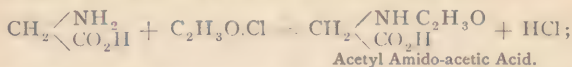
The aldehydes, too, can be converted into amido-acids by means of ammonium cyanide (*Ber.*, 14, 2686) (p. 151).

As the amido-acids contain both a carboxyl and an amido-group, they are acids and bases (amines). They afford salt-like derivatives with metallic oxides and with acids, and are capable also of directly combining with certain salts. Since, however, the carboxyl and amido-groups mutually neutralize each other, the amido-acids show neutral reaction, and it is very probable that both groups combine to produce an ammonium salt:—



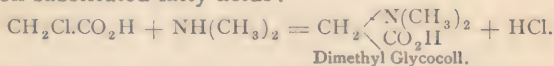
The existence and method of producing trimethyl glycolic acid or betaine would indicate this (p. 265). In the formation of the salts a separation of the two groups would again occur.

The hydrogen of the CO.OH group can be replaced by alcohol radicals with formation of *esters*, which are, however, unstable. On the other hand, hydrogen of the amido-group can be replaced by both acid and alcohol radicals. The *acid derivatives* appear when acid chlorides act upon the amido-acids or their esters:—



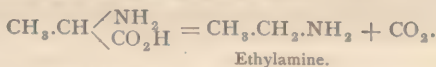
Acetyl Amido-acetic Acid.

whereas the *alcohol derivatives* are obtained by the action of the amines on substituted fatty acids:—



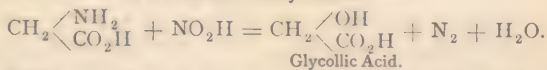
Dimethyl Glycocoll.

The alanines are crystalline bodies with usually a sweet taste, and are readily soluble in water. As a general thing they are insoluble in alcohol and ether. They are not affected by boiling alkalies, but when fused they decompose into salts of the fatty acids and into amines or ammonia. By dry distillation (with baryta especially) they yield amines and carbon dioxide:—



Ethylamine.

Nitrous acid converts them into oxy-acids:—



Glycollic Acid.

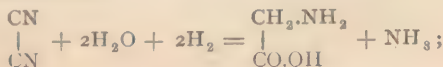
When KNO<sub>2</sub> is allowed to act on the HCl salts of the glycocoll esters, peculiar diazo-like compounds (p. 130), *e. g.*, diazo-acetic ester, CHN<sub>2</sub>.CO<sub>2</sub>.C<sub>2</sub>H<sub>5</sub> (*Ber.*, 17, 953), are formed.

Taurine, described p. 267, belongs to the amido-acids.

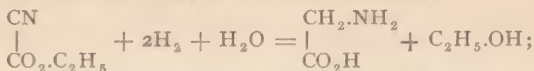
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Glycocoll,	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>
Alanine,	C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>
Propalanine,	C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>
Butalanine,	C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>
Leucine,	C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub> .

1. **Glycocoll**, Amido-acetic Acid, C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> = CH<sub>2</sub>(NH<sub>2</sub>).CO<sub>2</sub>H, is produced in the decomposition of various animal substances, like hippuric acid, glycocholic acid or glue (hence the name glycocoll: glucus, sweet; kolla, glue), when they are boiled with alkalies or acids. It is obtained synthetically: by heating monochloroacetic acid with ammonia; by conducting cyanogen gas into boiling hydriodic acid:—



furthermore, by the action of zinc and hydrochloric acid upon cyancarbonic ester (p. 295) in alcoholic solution :—



and finally, by letting ammonium cyanide and sulphuric acid act upon glyoxal,  $\text{CHO}\cdot\text{CHO}$  (p. 279), when the latter probably at first yields formaldehyde,  $\text{CH}_2\text{O}$  (*Ber.*, 15, 3087). Alanine is analogously formed from acetaldehyde and ammonium cyanide.

In preparing glycocoll, pour 2 parts concentrated  $\text{H}_2\text{SO}_4$  over finely divided glue (1 part), let stand several days, then add 8 parts of water and boil for some time, with occasional addition of water to replace the evaporated steam. Next, neutralize with chalk, filter and concentrate the filtrate. The glycocoll obtained in this manner is crystallized from hot, dilute alcohol, to free it of any adherent leucine.

A simpler procedure employs hippuric acid,  $\text{CH}_2\begin{array}{l} \text{NH}\cdot\text{C}_6\text{H}_5\text{O} \\ \text{CO}_2\text{H} \end{array}$  (benzoyl glycocoll). The latter is boiled with concentrated  $\text{HCl}$  (4 parts) for about one hour, allowed to cool, the separated benzoic acid filtered off, and the filtrate concentrated. The resulting glycocoll hydrochloride is boiled with water and lead oxide, the lead chloride filtered off and the excess of  $\text{Pb}$  precipitated by  $\text{H}_2\text{S}$ . In evaporating the filtered solution glycocoll crystallizes out.

Glycocoll is also obtained by warming monochloroacetic acid with dry ammonium carbonate (*Ber.*, 16, 2827).

Glycocoll crystallizes from water in large, rhombic prisms, which are soluble in 4 parts of cold water. It is insoluble in alcohol and ether. It possesses a sweetish taste, and melts with decomposition at  $232\text{--}236^\circ$ . Heated with baryta it breaks up into methylamine and  $\text{CO}_2$ ; nitrous acid converts it into glycollic acid. Ferric chloride imparts an intense red coloration to glycocoll solutions; acids discharge this, but ammonia restores it.

Glycocoll yields the following compounds with  $\text{HCl}$ :  $\text{C}_2\text{H}_5\text{NO}_2\cdot\text{HCl}$  and  $2(\text{C}_2\text{H}_5\text{NO}_2)\cdot\text{HCl}$ . The first is obtained with an excess of hydrochloric acid. It crystallizes in long prisms. The *nitrate*,  $\text{C}_2\text{H}_5\text{NO}_2\cdot\text{HNO}_3$ , forms large prisms.

An aqueous solution of glycocoll will dissolve many metallic oxides, forming salts. Of these the *copper salt*,  $(\text{C}_2\text{H}_4\text{NO}_2)_2\text{Cu} + \text{H}_2\text{O}$ , is very characteristic. It crystallizes in dark blue needles. The *silver salt*,  $\text{C}_2\text{H}_4\text{NO}_2\text{Ag}$ , crystallizes on standing over sulphuric acid. The combinations of glycocoll with salts, *e. g.*,  $\text{C}_2\text{H}_5\text{NO}_2\cdot\text{NO}_3\text{K}$ ,  $\text{C}_2\text{H}_5\text{NO}_2\cdot\text{NO}_3\text{Ag}$ , are mostly crystalline.

The *ethyl ester*,  $\text{CH}_2\begin{array}{l} \text{NH}_2 \\ \text{CO}_2\text{C}_2\text{H}_5 \end{array}$  (*Ber.*, 17, 957), is an oil with an odor resembling that of cacao, and boiling at  $149^\circ$ . It is very unstable and readily becomes an anhydride  $(\text{CH}_2(\text{NH})\text{CO})_2$  (*Ber.*, 16, 755). On leading  $\text{HCl}$  gas into glycocoll and absolute alcohol, the  $\text{HCl}$  salt is formed; this melts at  $144^\circ$ .

*Glycocollamide*,  $\text{CH}_2\begin{array}{l} \text{NH}_2 \\ \text{CO}_2\text{NH}_2 \end{array}$ , amidoacetamide, is produced when glycocoll is heated with alcoholic ammonia to  $160^\circ$ . A white mass, which dissolves readily in water, and reacts strongly alkaline. The  $\text{HCl}$  salt results on heating chloroacetic ester with alcoholic ammonia to  $70^\circ$ .

**Methyl-glycocoll**,  $C_3H_7NO_2 = CH_2 \begin{smallmatrix} \diagup NH.CH_3 \\ \diagdown CO_2H \end{smallmatrix}$ , **Sarcosine**, is obtained in the action of methylamine upon monochloracetic acid (p. 290), and is also produced when creatine and caffeine are heated with baryta. It crystallizes in rhombic prisms, which dissolve readily in water but with difficulty in alcohol. It melts at  $210-220^\circ$ , decomposing into  $CO_2$  and dimethylamine, yielding at the same time an anhydride,  $(C_3H_5NO)_2$ , which melts at  $150^\circ$  and boils at  $350^\circ$  (*Ber.*, 17, 286). It forms salts with acids; these have an acid reaction. Ignited with soda-lime it evolves methylamine. Nitrous acid changes it to the nitroso-compound,  $CH_2 \begin{smallmatrix} \diagup N.NO \\ \diagdown CO_2H \end{smallmatrix}.CH_3$ . Sarcosine affords methylhydantoin with cyanogen chloride.

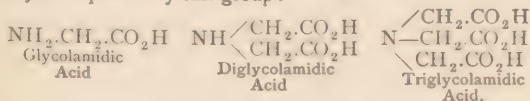
**Trimethylglycocoll**,  $CH_2 \begin{smallmatrix} \diagup N(CH_3)_3 \\ \diagdown CO.O \end{smallmatrix}$ , is betaine, described p. 265.

**Ethyl-glycocoll**,  $C_4H_9NO_2 = CH_2 \begin{smallmatrix} \diagup NH.C_2H_5 \\ \diagdown CO_2H \end{smallmatrix}$ , is obtained by heating monochloracetic acid with ethylamine. It consists of deliquescent leaflets; it unites with acids, bases and salts.

**Diethyl-glycocoll**,  $CH_2 \begin{smallmatrix} \diagup N(C_2H_5)_2 \\ \diagdown CO_2H \end{smallmatrix}$ , is derived from monochloracetic acid and diethylamine. It consists of deliquescent crystals which sublime under  $100^\circ$ .

**Aceto-glycocoll**,  $CH_2 \begin{smallmatrix} \diagup NH.C_2H_3O \\ \diagdown CO_2H \end{smallmatrix}$ , aceturic acid, is obtained by the action of acetyl chloride upon glycocoll silver, and of acetamide upon monochloracetic acid. It consists of small needles, which dissolve readily in water and alcohol, and char at  $130^\circ$ . It conducts itself like a monobasic acid.

Glycocoll may be viewed as ammonia with 1 hydrogen replaced by the monovalent group,  $-CH_2.CO_2H$ . It is plain that two and three hydrogen atoms in  $NH_3$  may be replaced by this group:—



These compounds are formed together with glycocoll on boiling monochloracetic acid with concentrated aqueous ammonia. The solution is concentrated, filtered off from the separated  $NH_4Cl$  and boiled with lead oxide. On cooling the lead salt of triglycolamidic acid separates out, while glycocoll and lead diglycolamidate remain dissolved. To remove the last compound,  $H_2S$  is added to the solution, and the filtrate boiled with zinc carbonate. Difficultly soluble zinc diglycolamidate separates out, while glycocoll remains dissolved.

Di- and triglycolamidic acids are crystalline compounds, forming salts with bases and acids; the first is dibasic, the second tribasic. Diglycolamidic acid yields a nitroso-compound with nitrous acid.

## 2. Amidopropionic Acids, $C_3H_7NO_2 = C_3H_5(NH_2)O_2$ .

(1) ***α*-Amidopropionic Acid**,  $CH_3.CH(NH_2).CO_2H$ , **Alanine**, is derived from *α*-chlor- and brom-propionic acid by means of ammonia, and from aldehyde ammonia by the action of  $CNH$  and  $HCl$  (p. 290). Aggregated, hard needles, with a sweetish



taste. The acid dissolves in 5 parts cold water and with more difficulty in alcohol; in ether it is insoluble. When carefully heated it melts and sublimes without decomposition, but heated rapidly it breaks up into ethylamine and carbon dioxide. Nitrous acid converts it into  $\alpha$ -lactic acid.

(2)  $\beta$ -**Amidopropionic Acid**,  $\text{CH}_2(\text{NH}_2).\text{CH}_2.\text{CO}_2\text{H}$ , is obtained from  $\beta$ -iodopropionic acid and  $\beta$ -nitropropionic acid (p. 290). It crystallizes in rhombic prisms which dissolve readily in water. When heated it sublimes with partial decomposition. Its copper compound is far more soluble than that of the isomeric alanine.

(3) **Amidobutyric Acids**,  $\text{C}_4\text{H}_7(\text{NH}_2)\text{O}_2$ .

$\alpha$ -**Amidobutyric Acid**,  $\text{CH}_3.\text{CH}_2.\text{CH}(\text{NH}_2).\text{CO}_2\text{H}$ , **Propalanine**, is obtained from brombutyric acid. It crystallizes in little leaflets or needles and is very soluble in water.

$\alpha$ -**Amidoisobutyric Acid**,  $(\text{CH}_3)_2\text{C}(\text{NH}_2).\text{CO}_2\text{H}$ , is made from acetonyleurea on heating with hydrochloric acid, and is obtained from acetone by means of  $\text{CNH}$ ,  $\text{NH}_3$  and  $\text{HCl}$  (p. 290). It is also produced in the oxidation of diacetaminine with chromic acid, (together with amido-isovaleric acid, p. 166). It crystallizes in large rhombic plates, and sublimes without decomposition near  $220^\circ$ .

(4)  $\alpha$ -**Amido-isovaleric Acid**,  $(\text{CH}_3)_2\text{CH}.\text{CH}(\text{NH}_2).\text{CO}_2\text{H}$ , **Butalanine**, occurs in the pancreas of the ox, and is formed on acting with ammonia upon brom-isovaleric acid. It consists of shining prisms, which sublime without fusing. It is more difficultly soluble in water and alcohol than leucine.

$\beta$ -**Amido-isovaleric Acid**,  $(\text{CH}_3)_2\text{C}(\text{NH}_2).\text{CH}_2.\text{CO}_2\text{H}$ , is obtained by the reduction of the nitro-acid (p. 184); it melts and sublimes at  $215^\circ$ .

(5)  $\alpha$ -**Amido-caproic Acid**,  $\text{CH}_3.(\text{CH}_2)_3.\text{CH}(\text{NH}_2).\text{CO}_2\text{H}$ , **Leucine**, occurs in different animal juices, in the pancreas, and is formed by the decay of albuminoids, or when they are boiled with alkalis or acids. Artificial leucine prepared from brom-caproic acid and valeric aldehyde appears to be an isomere of the preceding.

Leucine crystallizes in shining leaflets, which have a fatty feel, melt at  $170^\circ$  and sublime undecomposed when carefully heated. Rapid heating breaks it up into amylamine and  $\text{CO}_2$ . It is soluble in 27 parts of cold water and in hot alcohol.

Nitrous acid converts it into leucic acid (p. 288). Fused with potash it decomposes into ammonium and potassium valerates. When oxidized with lead peroxide we get valeronitrile,  $\text{C}_5\text{H}_{11}.\text{CN}$ .

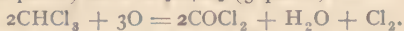
## CARBONIC ACID AND DERIVATIVES.

The acid exists only in its salts (p. 276), and may be regarded as oxyformic acid,  $\text{HO}.\text{CO}.\text{OH}$ . Its symmetrical structure distinguishes it, however, from the other oxy-acids with three atoms of oxygen. It is a weak *dibasic* acid and constitutes the transition to

the true dibasic dicarboxylic acids—hence it will be treated separately.

**Carbon Monoxide**, CO, and **Carbon Dioxide**, CO<sub>2</sub>, the anhydride of carbonic acid, have already received mention in the inorganic chemistry. Paper moistened with a solution of palladium chloride is blackened by CO, hence it may be employed as a reagent for this latter compound.

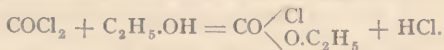
**Carbonyl Chloride**, COCl<sub>2</sub>, Phosgene Gas, is formed by the direct union of CO with Cl<sub>2</sub> in sunlight (they combine very slowly in diffused light); by conducting CO into boiling SbCl<sub>5</sub>, and by oxidizing chloroform (2 parts) with a mixture of concentrated sulphuric acid (50 parts) and Cr<sub>2</sub>O<sub>7</sub>K<sub>2</sub> (5 parts):—



The simplest course is to conduct CO and Cl<sub>2</sub> over pulverized and cooled bone charcoal (Paterno). Instead of condensing the gas it may be collected in cooled benzene. To remove excess of chlorine the COCl<sub>2</sub> is passed over heated antimony.

Carbonyl chloride is a colorless gas with suffocating odor, and on cooling is condensed to a liquid which boils at +8°. Water at once breaks it up into CO<sub>2</sub> and 2HCl.

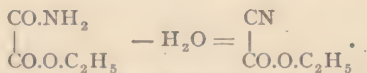
When phosgene gas is allowed to act upon anhydrous alcohols, the esters of **chlorcarbonic acid** are formed:—



They are more correctly esters of **chlorformic acid**, CCIO.OH (p. 175). These are volatile, disagreeable-smelling liquids, decomposable by water. When heated with anhydrous alcohols they afford the neutral carbonic esters.

The methyl ester, CCIO.O.CH<sub>3</sub>, boils at 71.4°, the ethyl ester, CCIO<sub>2</sub>.C<sub>2</sub>H<sub>5</sub>, at 94°, the propyl ester, at 115°, the isobutyl ester at 128.8°, and the isoamyl ester, at 154° (*Ber.*, 13, 2417).

**Ethyl Cyancarbonic Ester**, CO < <sup>CN</sup> O.C<sub>2</sub>H<sub>5</sub>, or cyanformic ester, is obtained by distilling oxamic ester with P<sub>2</sub>O<sub>5</sub>, or better, with PCl<sub>5</sub>:—



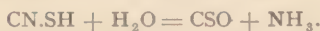
It is a pungent-smelling liquid, boiling at 115–116°. It is insoluble in water, but is gradually decomposed by the latter into CO<sub>2</sub>, CNH and alcohol. Zinc and hydrochloric acid convert it into glycocoll (p. 291). Concentrated hydrochloric acid decomposes it into oxalic acid and ammonium chloride. Bromine or anhydrous HCl at 100° converts it into a crystalline, polymeric modification which melts at 165°, and by the action of alkalis in the cold is transformed into salts of paracyancarbonic acid, *e.g.*, (CN.CO<sub>2</sub>K)<sub>n</sub>.

The methyl ester, CN.CO<sub>2</sub>.CH<sub>3</sub>, boils at 100–101°.



Carbon mono-sulphide, analogous to carbon monoxide, is unknown.

**Carbon Oxysulphide**, COS, occurs in some mineral springs, and is formed in various ways, as, for example, by conducting sulphur vapor and carbon monoxide through red hot tubes. It is most easily prepared by heating potassium thiocyanate with sulphuric acid, diluted with some water:—

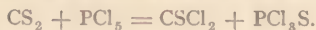


In order to obtain it pure, conduct the gas into an alcoholic potash solution, and decompose the separated potassium ethyl thio-carbonate,  $\text{CO} \begin{smallmatrix} \text{O.C}_2\text{H}_5 \\ \text{SK} \end{smallmatrix}$  (p. 300), with dilute hydrochloric acid.

Carbon oxysulphide is a colorless gas, with a faint and peculiar odor. It ignites readily, and forms an explosive mixture with air. It is soluble in an equal volume of water. It is decomposed by the alkalis according to the following equation:—



**Thiocarbonyl Chloride**,  $\text{CSCl}_2$ , is produced when Cl acts upon  $\text{CS}_2$ , and when  $\text{CS}_2$  is heated with  $\text{PCl}_5$  in closed tubes to  $200^\circ$ :—



It is a pungent, red-colored liquid, insoluble in water, and boiling at  $70^\circ$ . On standing exposed to sun light, it is converted into a polymeric, crystalline compound which melts at  $112^\circ$ , and at  $180^\circ$  reverts to the liquid body.

**Carbon Disulphide**,  $\text{CS}_2$ , is obtained by conducting sulphur vapor over ignited charcoal. It is a colorless liquid, with strong refractive power, boils at  $47^\circ$ , and at  $0^\circ$  has a specific gravity of 1.297. It is obtained pure by distilling the commercial product over mercury or mercuric chloride; its odor is then very faint. It is almost insoluble in water, but mixes with alcohol and ether. It serves as an excellent solvent for iodine, sulphur, phosphorus, fatty oils and resins. In the cold it combines with water, yielding the hydrate  $2\text{CS}_2 + \text{H}_2\text{O}$ , which decomposes again at  $-3^\circ$ .

To detect slight quantities of carbon disulphide it is converted, by means of alcoholic potash, into potassium xanthate, and this into the copper salt (p. 299). The production of the bright-red compound of  $\text{CS}_2$  with triethyl phosphine (p. 133, and *Berichte*, 13, 1732) is a more delicate test.

Dry chlorine gas converts  $\text{CS}_2$  into sulphur monochloride and thio-carbonyl chloride,  $\text{CSCl}_2$ . By the addition of chlorine we obtain  $\text{CSCl}_4 = \text{CCl}_3.\text{SCl}$ , a yellow liquid, which boils at  $146^\circ$ , and becomes  $\text{CCl}_3.\text{SO}_2\text{Cl}$  (p. 120) when oxidized. Zinc and hydrochloric acid convert  $\text{CS}_2$  into  $\text{CSH}_2$  (p. 153).

Carbon disulphide can be called the sulphanydride of tri-thio-carbonic acid,  $\text{CS}_3\text{H}_2$ . It is perfectly analogous to  $\text{CO}_2$ , and unites with metallic sulphides, forming tri-thiocarbonates.



**Tri-thiocarbonic Acid**,  $\text{CS}_3\text{H}_2 = \text{CS} \begin{smallmatrix} \text{SH} \\ \text{SH} \end{smallmatrix}$ . Hydrochloric acid precipitates this as a reddish-brown, oily liquid, from solutions of its alkali salts. The sodium salt,  $\text{CS}_3\text{Na}_2$ , separates in the form of a thick, red liquid when alcohol and ether are added to a solution of sodium sulphide containing carbon disulphide. This salt is readily dissolved by water. The barium salt,  $\text{CS}_3\text{Ba}$ , is a yellow crystalline powder, obtained by shaking aqueous  $\text{BaS}$  with  $\text{CS}_2$ .

**Ethyl Trithiocarbonate**,  $\text{CS} \begin{smallmatrix} \text{S.C}_2\text{H}_5 \\ \text{S.C}_2\text{H}_5 \end{smallmatrix}$ , is formed when an alcoholic solution of ethyl iodide acts upon sodium trithiocarbonate. It is a yellow oil, insoluble in water, and boils at  $240^\circ$ . It affords red colored, crystalline derivatives with 2 atoms of Cl or Br. These regenerate the ether when treated with water. The methyl ester,  $\text{CS}(\text{S.CH}_3)_2$ , boils at  $204\text{--}205^\circ$ . The action of ethylene bromide upon the sodium salt yields the *ethylene ester*,  $\text{CS} \begin{smallmatrix} \text{S} \\ \text{S} \end{smallmatrix} \text{C}_2\text{H}_4$ ; large, yellow crystals, melting at  $36.5^\circ$ . These are readily soluble in ether, more difficultly so in alcohol. When oxidized with dilute nitric acid the ester becomes ethylene-dithiocarbonic ester,  $\text{COS}_2\text{:C}_2\text{H}_4$ , which forms plates, melting at  $31^\circ$ .

**Ethyl-trithiocarbonic Acid**,  $\text{CS} \begin{smallmatrix} \text{S.C}_2\text{H}_5 \\ \text{SH} \end{smallmatrix}$ , is not known in a free condition. The *potassium salt*,  $\text{CS} \begin{smallmatrix} \text{S.C}_2\text{H}_5 \\ \text{SK} \end{smallmatrix}$ , is produced by the direct union of  $\text{CS}_2$  with potassium mercaptide,  $\text{C}_2\text{H}_5\text{:SK}$ .

Dithiocarbonic acid,  $\text{COS}_2\text{H}_2$ , may have one of two formulas:—

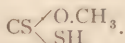


Dithiocarbonic Acid



Thiosulphocarbonic Acid.\*

The free acids are not known; dialkyl esters, however, do exist. Thiosulphocarbonic acid is capable of forming esters or ether acids of the type  $\text{CS} \begin{smallmatrix} \text{O.C}_2\text{H}_5 \\ \text{SH} \end{smallmatrix}$ , called *xanthic acids*:—

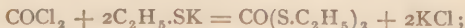


Methyl Xanthate

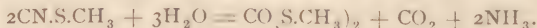


Ethyl Xanthic Acid.

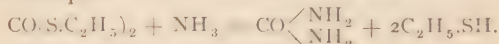
The esters of *dithiocarbonic acid*,  $\text{CO}(\text{SH})_2$ , result when  $\text{COCl}_2$  acts upon the mercaptides:—



and when thiocyanic esters (p. 239) are heated with concentrated sulphuric acid:—



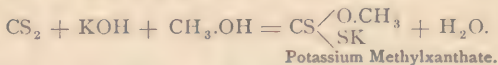
They are liquids with garlicky odor. Alcoholic ammonia decomposes them into urea and mercaptans:—



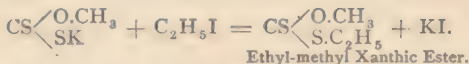
\* To distinguish the isomerides the sulphur joined with two valences to carbon is called *sulpho*-, the monovalent sulphur, *thio*.

The *methyl ester*,  $\text{CO}(\text{S}.\text{CH}_3)_2$ , boils at  $169^\circ$ ; the *ethyl ester*,  $\text{CO}(\text{S}.\text{C}_2\text{H}_5)_2$ , at  $196^\circ$ .

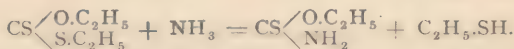
The **xanthates**,  $\text{R.O.CS.SM}'$ , are produced by the combined action of  $\text{CS}_2$  and caustic alkalies in alcoholic solutions:—



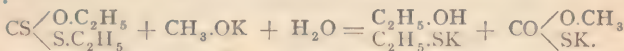
Cupric salts precipitate *yellow* copper salts from solutions of alkali xanthates. By the action of alkyl iodides upon the salts we obtain the esters:—



The esters are liquids, insoluble in water. Ammonia breaks them up into mercaptans and esters of sulphocarbamic acid (p. 302):



With alkali alcoholates, mercaptan and alcohol separate, and salts of the alkyl thiocarbonic acids (p. 300) are formed (*Ber.*, 13, 530):—



**Xanthic Acid**, or ethyl oxydithiocarbonic acid,  $\text{C}_2\text{H}_5.\text{O.CS.SH}$ . A heavy liquid, not soluble in water. It decomposes at  $25^\circ$  already into alcohol and  $\text{CS}_2$ .

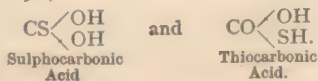
**Potassium Xanthate**,  $\text{C}_2\text{H}_5.\text{O.CS.SK}$ , forms on mixing alcoholic potash with  $\text{CS}_2$ . It consists of silky needles, which dissolve very readily in water, and are quite insoluble in alcohol. The salts of the heavy metals are insoluble in water, and are obtained from the potassium salt by double decomposition. The copper salt is yellow; it decomposes on drying.

**Xanthic Disulphide**,  $\text{S.CS.O.C}_2\text{H}_5$ , is produced on adding an alcoholic solution of iodine to the potassium salt (p. 203). Insoluble, shining needles, which melt at  $28^\circ$ .

When ethyl chloride acts upon potassium xanthate, we get the ethyl ester,  $\text{C}_2\text{H}_5.\text{O.CS.S.C}_2\text{H}_5$ , a colorless oil, which boils at  $200^\circ$ .

The remaining alkyl oxydithiocarbonic acids are perfectly similar to xanthic acid. Ethyl-methyl xanthic ester,  $\text{CH}_3.\text{O.CS.S.C}_2\text{H}_5$ , and methyl xanthic ester,  $\text{C}_2\text{H}_5.\text{O.CS.S.CH}_3$ , both boil at  $184^\circ$ . Their behavior with ammonia and sodium alcoholate (see above) distinguishes them.

Carbonic acid containing one sulphur atom may exist in two isomeric forms (p. 298):—



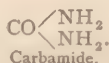
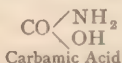
Both acids are incapable of existing free, but they afford isomeric dialkyl esters. Thiocarbonic acid can, like xanthic acid, yield ether-thiocarbonates of the type,  $\text{CO} \begin{smallmatrix} \text{O.C}_2\text{H}_5 \\ \text{SK} \end{smallmatrix}$ .

**Sulphocarbonic Acid.** Its *ethyl ester*,  $\text{CS}(\text{O.C}_2\text{H}_5)_2$ , is produced by the action of sodium alcoholate upon thiocarbonyl chloride,  $\text{CSCl}_2$ , and in the distillation of  $\text{S}_2(\text{CS.O C}_2\text{H}_5)_2$ , see above. It is an ethereal smelling liquid, which boils at  $161-162^\circ$ . With alcoholic ammonia the ester decomposes into alcohol and ammonium thiocyanate,  $\text{CN.S.NH}_4$ ; alcoholic potash converts it into alcohol and potassium ethyl thiocarbonate.

**Ethyl Thiocarbonic Acid.** The *potassium salt*,  $\text{CO} \begin{smallmatrix} \text{O.C}_2\text{H}_5 \\ \text{SK} \end{smallmatrix}$ , is obtained from xanthic esters with alcoholic potash (p. 299), and in the union of  $\text{CO}_2$  with potassium mercaptide,  $\text{C}_2\text{H}_5\text{.SK}$ . It crystallizes in needles and prisms, which readily dissolve in water and alcohol. With ethyl iodide the potassium salt forms *ethyl thioxycarbonate*, which can be prepared from chlorcarbonic ester,  $\text{COCl.O.C}_2\text{H}_5$ , and sodium mercaptide. It boils at  $156^\circ$ . Alkalies decompose it into carbonate, alcohol and mercaptan.

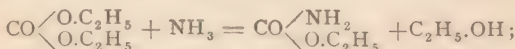
## AMIDE DERIVATIVES OF CARBONIC ACID.

Carbonic acid is dibasic, and forms amide derivatives similar to those of the dibasic dicarboxylic acids:—

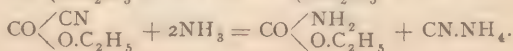
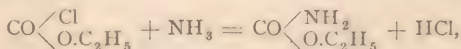


**Carbamic Acid**,  $\text{H}_2\text{N.CO.OH}$ , is not known in a free state. It seems its ammonium salt is contained in commercial ammonium carbonate, and is prepared by the direct union of  $2\text{NH}_3$  with  $\text{CO}_2$ . It is a white mass which breaks up at  $60^\circ$  into  $2\text{NH}_3$  and  $\text{CO}_2$ , but these combine again upon cooling. Salts of the earth and heavy metals do not precipitate the aqueous solution; it is only after warming that carbonates separate, when the carbamate has absorbed water and become ammonium carbonate. When ammonium carbamate is heated to  $130-140^\circ$  in sealed tubes, water is withdrawn and urea,  $\text{CO}(\text{NH}_2)_2$ , formed.

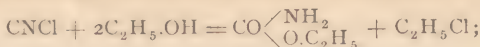
The *esters* of carbamic acid are called *urethanes*; these are obtained by the action of ammonia at ordinary temperatures upon carbonic esters:—



and in the same manner from the esters of chlorcarbonic and cyan-carbonic acids:—



Also by conducting cyanchloride into the alcohols:—

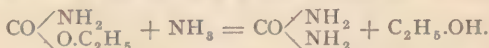


and by the direct union of cyanic acid with the alcohols:—



When there is an excess of cyanic acid employed, allophanic esters are produced at the same time.

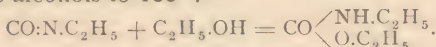
The urethanes are crystalline, volatile bodies, soluble in alcohol, ether and water. Alkalies decompose them into  $\text{CO}_2$ , ammonia, and alcohols. They afford urea when heated with ammonia:—



Conversely, on heating urea or its nitrate with alcohols, the urethanes are regenerated.

**Methyl Carbamic Ester**,  $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \diagdown \\ \text{O.CH}_3 \end{smallmatrix}$ , methyl urethane, crystallizes in plates which melt at  $52^\circ$ , and boil at  $177^\circ$ . The *ethyl ester*,  $\text{CO}(\text{NH}_2)\cdot\text{O.C}_2\text{H}_5$ , also called urethane, consists of large plates, which melt at  $47\text{--}50^\circ$ , and boil at  $180^\circ$ . The *propyl ester* melts at  $53^\circ$ , and boils at  $195^\circ$ . The *isoamyl ester* crystallizes from water in silky needles, which melt at  $60^\circ$ , and boil at  $220^\circ$ .

Alcohol radicals may also replace the hydrogen of  $\text{NH}_2$  in carbamic acid. The esters of these alkylized carbamic acids are formed, like the urethanes, by the action of carbonic or chlorcarbonic esters upon amines; and on heating isocyanic esters (p. 236) with the alcohols to  $100^\circ$ :—

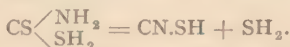


**Ethyl Etho-carbamic Ester**,  $(\text{C}_2\text{H}_5)\text{HN.CO.O.C}_2\text{H}_5$ , boils at  $174\text{--}175^\circ$ .

Cyanic acid (p. 233) is probably the imide of carbonic acid—**Carbimide**,  $\text{CO:NH}$ .

Perfectly analogous amides are derived from the thio-carbonic acids.

**Dithiocarbamic Acid**,  $\text{CS} \begin{smallmatrix} \text{NH}_2 \\ \diagdown \\ \text{SH} \end{smallmatrix}$ , is a reddish oil, obtained by decomposing the ammonium salt with dilute sulphuric acid. It breaks up very readily into thiocyanic acid and hydrogen sulphide:—

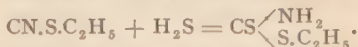


Water decomposes it into cyanic acid and  $2\text{SH}_2$ . The *ammonium salt*,  $\text{CS} \begin{smallmatrix} \text{NH}_2 \\ \diagdown \\ \text{S.NH}_4 \end{smallmatrix}$ , affords yellow needles or prisms, and is produced in the action of alcoholic ammonia upon  $\text{CS}_2$ .



By heating this salt together with aldehyde we obtain the compound,  $\text{H}_2\text{N}.\text{CS}.\text{S.N}(\text{CH}_3.\text{CH})_2 = \text{C}_5\text{H}_{10}\text{S}_2\text{N}_2$ , *carbothialdine*. This is also obtained on mixing  $\text{CS}_2$  with alcoholic aldehyde-ammonia. It consists of large, shining crystals, and when boiled with acids decomposes into  $\text{NH}_3$ ,  $\text{CS}_2$ , and aldehyde.

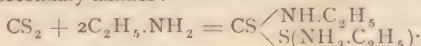
The **dithiourethanes** are the esters of the above acid. They arise when the thiocyanic esters are heated with  $\text{H}_2\text{S}$  (compare phenyl dithiocarbamic acid):—



They are crystalline compounds, soluble in alcohol and ether, and are decomposed into ammonium thiocyanate and mercaptans, when treated with alcoholic ammonia.

The *ethyl ester* melts at  $41-42^\circ$  and the *propyl ester* at  $97^\circ$ . Both crystallize in shining leaflets.

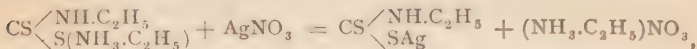
Alkyls may replace hydrogen of  $\text{NH}_2$  in dithiocarbamic acid. The amine salts of these compounds are obtained on heating  $\text{CS}_2$  with alcoholic solutions of the primary and secondary amines:—



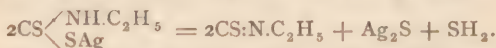
Boiling aqueous soda eliminates ethylamine from this salt and gives us sodium ethyl dithiocarbamic acid,  $\text{CS} \begin{array}{c} \text{NH.C}_2\text{H}_5 \\ \text{SNa} \end{array}$ . The free acid obtained from this is an oil which solidifies to a crystalline mass. When its amine salts are heated to  $110^\circ$ , dialkyl thio-ureas are produced (p. 311):—



If the aqueous solution of the salts obtained from the primary amines be heated with metallic salts, *e. g.*,  $\text{AgNO}_3$ ,  $\text{FeCl}_3$  or  $\text{HgCl}_2$ , salts of ethyl-dithiocarbamic acid are precipitated:—

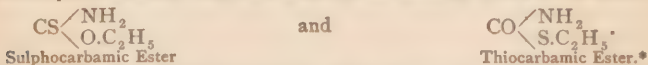


which, when boiled with water, afford the mustard oils (p. 240):—

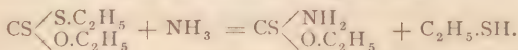


The salts obtained from the secondary amines do not yield mustard oils (*Berichte*, 8, 107).

Monosulphur carbamic acid can occur in two isomeric forms in its esters:—



(1) The esters of **sulphocarbamic acid**—thiourethanes—are formed when alcoholic ammonia acts upon the xanthic esters (p. 298):—



\* Imidothiocarbamic acid,  $\text{HN:C} \begin{array}{c} \text{OH} \\ \text{SH} \end{array}$ , is isomeric with these acids. It is only known in its phenyl derivatives (see phenyl isothiourethane).

They are crystalline compounds, which decompose into mercaptans, cyanic acid and cyanuric acid on heating. Alcoholic alkalis decompose them into alcohols and thiocyanates, CNSK.

The *ethyl ester* of sulphocarbamic acid is slightly soluble in water and melts at  $38^{\circ}$ . The *methyl ester* melts at  $43^{\circ}$ .

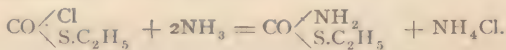
The esters from alkylic sulphocarbamic acids are obtained from the mustard oils on heating with anhydrous alcohols to  $110^{\circ}$  :—



They are liquids with an odor like that of leeks, and decompose into alcohols,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and alkylamines, when acted upon with alkalis or acids.

*Ethyl Etho-sulphocarbamic Ester*,  $\text{C}_2\text{H}_5.\text{NH.CS.O.C}_2\text{H}_5$ , boils at  $204\text{--}208^{\circ}$ . Allyl sulphocarbamic ester,  $\text{C}_3\text{H}_5.\text{NH.CS.O.C}_2\text{H}_5$ , from allyl mustard oil, boils at  $210\text{--}215^{\circ}$ .

(2) The esters of **thiocarbamic acid** are obtained by conducting HCl into a solution of CNSK (or of alkyl sulphocyanates, *Ber.*, **14**, 1083) in alcohols (together with esters of sulphocarbamic acid—*Journ. pract. Chem.*, **16**, 358); and by the action of ammonia upon the dithiocarbonic esters,  $\text{CO}(\text{S.C}_2\text{H}_5)_2$ , and chlorthioformic esters :—



These are crystalline compounds, which are difficultly soluble in water and that decompose when heated.

The *methyl ester*,  $\text{NH}_2.\text{CO.S.CH}_3$ , melts at  $95\text{--}98^{\circ}$ . The *ethyl ester* melts at  $108^{\circ}$  ( $102^{\circ}$ ).

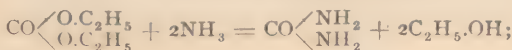
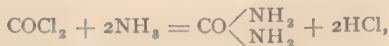
*Ammonium Thiocarbonate*,  $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{S.NH}_4 \end{smallmatrix}$ , is prepared by leading COS into alcoholic ammonia. It is a colorless, crystalline mass, becoming yellow on exposure to the air, owing to the formation of ammonium sulphide. When heated to  $130^{\circ}$  it breaks up into  $\text{H}_2\text{S}$  and urea.

### Carbamide, Urea, $\text{CH}_4\text{N}_2\text{O} = \text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$ .

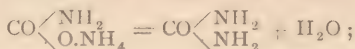
This was discovered in urine in 1773, and was first synthesized by Wöhler in 1828. It occurs in various animal fluids, chiefly in the urine of mammals, birds, and some reptiles. It may be prepared artificially in various ways: (1) by evaporating the aqueous solution of ammonium isocyanate, when an atomic transposition occurs (Wöhler) :—



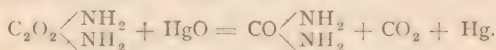
(2) by the action of ammonia upon carbonyl chloride or carbonic esters :—



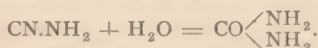
(3) by heating ammonium carbamate or thiocarbamate to 130–140° :—



(4) by heating oxamide with mercuric oxide :—



It is further produced in the action of alkalies upon creatine and allantoin; in the oxidation of uric acid, guanine and xanthine, and when small quantities of acids act upon cyanamide (p. 247) :—

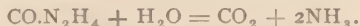


*Preparation from Urine.* Urine is evaporated to a thick syrup, and when cool concentrated nitric acid (or, better, oxalic acid) is poured over it. The separated, brown-colored nitrate is repeatedly crystallized from dilute nitric acid, in order to obtain it pure, after which it is dissolved in water, heated with barium carbonate, and the filtrate evaporated to dryness, and the urea extracted from the residue with absolute alcohol.

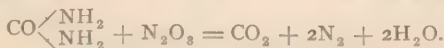
The best synthetic method is its preparation from ammonium cyanate. Mixed aqueous solutions of potassium cyanate and ammonium sulphate (in equivalent quantities) are evaporated; on cooling potassium sulphate crystallizes out and is filtered off, the filtrate being evaporated to dryness, and the urea extracted by means of hot alcohol. The following has been found to afford good practical results: 28 parts anhydrous yellow prussiate of potash are fused with 14 parts  $\text{MnO}_2$ ; the fused mass is dissolved in water, 20½ parts ammonium sulphate added, the whole is then evaporated to dryness and the urea extracted from the residue with alcohol.

The easiest course in obtaining urea is to conduct  $\text{NH}_3$  into fused phenyl carbonate,  $\text{CO}(\text{O.C}_6\text{H}_5)_2$  (*Berichte*, 17, 1286).

Urea crystallizes in long, rhombic prisms or needles, which possess a cooling taste, like that of saltpetre. It dissolves in 1 part cold water and in 5 parts of alcohol; it is almost insoluble in ether. It melts at 132°, and above that breaks up into ammonia, ammelide, biuret and cyanuric acid. When urea is heated above 100° with water, or when boiled with alkalies or acids, it decomposes into its constituents :—



Nitrous acid decomposes urea, as it does all other amides :—



Urea affords crystalline compounds with acids, bases and salts. Although it is a diamide it combines with but one equivalent of acid (one of the amido-groups is neutralized by the carbonyl group).

*Urea Nitrate*,  $\text{CH}_4\text{N}_2\text{O.HNO}_3$ , crystallizes in shining leaflets, which are not very soluble in nitric acid. The *HCl salt*,  $\text{CH}_4\text{N}_2\text{O.HCl}$ , is formed when dry HCl is conducted over urea; it is a yellow oil, which suffers decomposition on exposure. The *oxalate*,  $(\text{CH}_4\text{N}_2\text{O})_2\text{C}_2\text{H}_2\text{O}_4 + 2\text{H}_2\text{O}$ , is precipitated by oxalic

acid from an aqueous solution of urea in the form of thin leaflets, which are not readily soluble in water.

The compound with mercuric oxide,  $\text{CH}_4\text{N}_2\text{O} \cdot 2\text{HgO}$ , is a white precipitate, obtained on adding KOH and mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2$ , to a urea solution. It becomes yellow in color when washed with water, and has then the composition expressed by the formula,  $\text{CH}_4\text{N}_2\text{O} \cdot 3\text{HgO}$ . Silver oxide yields a crystalline, gray compound,  $(\text{CH}_4\text{N}_2\text{O})_2 \cdot 3\text{Ag}_2\text{O}$ .

On evaporating a solution containing both urea and sodium chloride, the compound,  $\text{CH}_4\text{N}_2\text{O} \cdot \text{NaCl} + \text{H}_2\text{O}$ , separates in shining prisms. Large rhombic prisms of  $\text{CH}_4\text{N}_2\text{O} \cdot \text{AgNO}_3$  crystallize from a concentrated solution of urea and silver nitrate.

Mercuric nitrate precipitates compounds of variable composition from aqueous urea; a volumetric method for estimating the latter is founded on this fact.

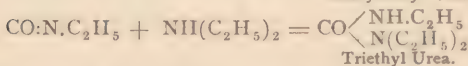
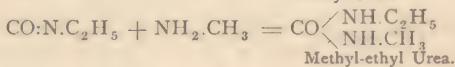
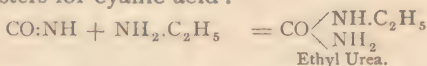
**Isuret**,  $\text{HN}:\text{CH}.\text{NH}.\text{OH}$ , is isomeric with urea; it is produced by the direct union of hydroxylamine,  $\text{NH}_3\text{O}$  with  $\text{CNH}$  (p. 250).

**Hydroxy-urea**,  $\text{CO} \begin{smallmatrix} \text{NH}.\text{OH} \\ \text{NH}_2 \end{smallmatrix}$ , is obtained by mixing aqueous hydroxylamine nitrate with potassium isocyanate. It is readily soluble in water and alcohol, but is thrown out of these solutions in rhombic leaflets by ether. It melts at  $128-130^\circ$ .

## COMPOUND UREAS.

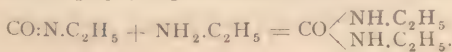
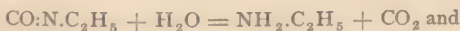
By this term we designate all compounds derived from urea by the replacement of hydrogen in the amido-groups by alcohol or acid radicals.

1. *Alkyl*ic ureas are produced according to the same reactions which afforded urea, substituting, however, amine bases for ammonia or isocyanic esters for cyanic acid:—



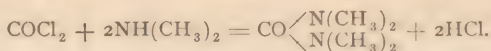
The primary and secondary amines react thus, but not the tertiary amines.

Alkylc ureas are formed, too, when isocyanic esters are heated with water— $\text{CO}_2$ , and amines being produced; the latter unite with the esters:—

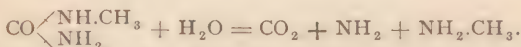




The action of  $\text{COCl}_2$  upon the secondary amines affords them :—



Ureas of this class are perfectly analogous to ordinary urea as regards their properties and reactions. They generally form salts with one equivalent of acid. Excepting those containing four alkyl groups, they are crystalline solids. On heating those with one alkyl group, cyanic acid (or cyanuric acid) and an amine are produced. The higher alkylized members can be distilled without decomposition. Boiling alkalies convert them all into  $\text{CO}_2$  and amines :—



**Ethyl Urea**,  $\text{CO} \begin{smallmatrix} \text{NH}.\text{C}_2\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$ , forms large prisms, melting at  $92^\circ$ . They dissolve readily in water and alcohol. Nitric acid does not throw them out of aqueous solution.

**$\alpha$ -Diethyl Urea**,  $\text{CO} \begin{smallmatrix} \text{NH}.\text{C}_2\text{H}_5 \\ \text{NH}.\text{C}_2\text{H}_5 \end{smallmatrix}$ , crystallizes in long prisms, melting at  $112^\circ$ , and boiling undecomposed at  $263^\circ$ . Nitrous acid (or  $\text{KNO}_2$  upon the sulphate) changes it to *nitrosodiethyl urea*,  $\text{CO} \begin{smallmatrix} \text{NH}.\text{C}_2\text{H}_5 \\ \text{N}(\text{NO}).\text{C}_2\text{H}_5 \end{smallmatrix}$ . This is a yellow oil, that solidifies on cooling, and melts at  $+5^\circ$ . By reduction, it yields an amido-derivative, which breaks up into  $\text{CO}_2$ , ethylamine, and ethyl hydrazine (p. 130).

**$\beta$ -Diethyl Urea**,  $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{N}(\text{C}_2\text{H}_5)_2 \end{smallmatrix}$ , is formed when cyanic acid acts upon diethylamine.

**Triethyl Urea**,  $\text{CO} \begin{smallmatrix} \text{NH}.\text{C}_2\text{H}_5 \\ \text{N}(\text{C}_2\text{H}_5)_2 \end{smallmatrix}$ , melts at  $63^\circ$ , and distils at  $223^\circ$ ; it is very soluble in water, alcohol and ether.

**Tetraethyl Urea**,  $\text{CO} \begin{smallmatrix} \text{N}(\text{C}_2\text{H}_5)_2 \\ \text{N}(\text{C}_2\text{H}_5)_2 \end{smallmatrix}$ , is produced on conducting  $\text{COCl}_2$  into a solution of diethylamine in benzene :—



This liquid boils at  $210$ – $215^\circ$ , and has an odor resembling that of peppermint. It is soluble in acids, but is thrown out of solution again by alkalies.

**Diallyl Urea**,  $\text{CO} \begin{smallmatrix} \text{NH}.\text{C}_3\text{H}_5 \\ \text{NH}.\text{C}_3\text{H}_5 \end{smallmatrix}$ , Sinapoline, is formed when alkyl isocyanic ester is heated with water (p. 305) :—



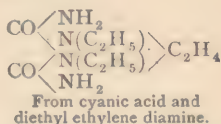
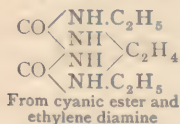
or by heating mustard oil with water and lead oxide. Diallyl-thio-urea is first formed, but the lead oxide desulphurizes it (p. 311). Diallyl-urea crystallizes in large, brilliant leaflets, which melt at  $100^\circ$ . They are not readily soluble in water, and have an alkaline reaction.

**Allyl Urea**,  $\text{CO} \begin{smallmatrix} \text{NH}.\text{C}_3\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$ , is obtained from allyl cyanic ester and ammonia or from allylamine sulphate and potassium cyanate. It affords beautiful prisms, melting at  $85^\circ$ .

**Ethylene Diurea**,  $\text{CO} \begin{array}{c} \diagup \text{NH}_2 \\ \text{NH} \\ \diagdown \text{NH}_2 \end{array} \text{C}_2\text{H}_4$ , is produced by heating ethylene dia-

mine hydrochloride with silver cyanate. It is difficultly soluble in alcohol, but readily in hot water. It melts at  $192^\circ$  with decomposition.

Ethylated ethylene ureas are similarly formed:—



Derivatives of urea with *aldehyde radicals* exist. They are produced at ordinary temperatures by the union of urea with aldehydes, with the elimination of water.

**Ethidene Urea**,  $\text{CO} \begin{array}{c} \diagup \text{NH} \\ \text{NH} \\ \diagdown \end{array} \text{CH.CH}_3$ , is not very soluble in water, and melts at  $154^\circ$ . **Chloral Urea**,  $\text{CO}(\text{NH})_2:\text{CH.CCl}_3$ , crystallizes in leaflets which melt at  $150^\circ$  with decomposition.

When boiled with water these compounds break up into aldehydes and urea.

## 2. DERIVATIVES OF UREA WITH ACID RADICALS, OR UREÏDES.

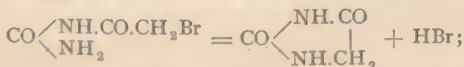
The derivatives of the monobasic acids are obtained in the action of acid chlorides or acid anhydrides upon urea. By this procedure, however, it is possible to introduce but one radical. The compounds are solids; they decompose when heat is applied to them, and are incapable of forming salts with acids. Alkalies cause them to separate into their components.

**Acetyl Urea**,  $\text{CO} \begin{array}{c} \diagup \text{NH.C}_2\text{H}_3\text{O} \\ \text{NH}_2 \end{array}$ , is not very soluble in cold water and alcohol. It forms long, silky needles, which melt at  $112^\circ$ . Heat breaks it up into acetamide and isocyanuric acid. *Chloracetyl urea*,  $\text{H}_2\text{N.CO.NH.CO.CH}_2\text{Cl}$ , from urea and chloracetyl chloride, crystallizes in fine needles, which decompose about  $160^\circ$ . *Bromacetyl urea* is difficultly soluble in water. When heated with ammonia it becomes hydantoin (see below).

**Diacetyl Urea**,  $\text{CO} \begin{array}{c} \diagup \text{NH.C}_2\text{H}_3\text{O} \\ \text{NH.C}_2\text{H}_3\text{O} \end{array}$ , results when  $\text{COCl}_2$  acts on acetamide,  $\text{NH}_2.\text{C}_2\text{H}_3\text{O}$ , and sublimes in needles without decomposition.

*Derivatives of Urea with divalent Acids:—*

**Glycolyl Urea**,  $\text{C}_3\text{H}_4\text{N}_2\text{O}_2$ , **Hydantoin**, is produced by heating bromacetyl urea with alcoholic ammonia:—



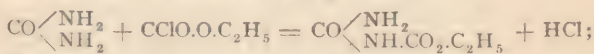
and from allantoin, and from alloxanic acid by heating with hydriodic acid. It crystallizes from hot water and alcohol, in needles,



on heating acetone and potassium cyanide (containing potassium isocyanate) with fuming hydrochloric acid. It is very soluble in water, and crystallizes in large prisms which melt at  $175^{\circ}$  and sublime in needles. When heated to  $160^{\circ}$  with fuming hydrochloric acid, it breaks up into  $\alpha$ -oxyisobutyric acid,  $\text{NH}_3$  and  $\text{CO}_2$ . Boiling with baryta water converts it into acetonyluric acid,  $\text{H}_2\text{N.CO.NH.C}(\text{CH}_3)_2.\text{CO}_2\text{H}$ , which fuses at  $155\text{--}160^{\circ}$ .

The ureides of the dibasic acids and those of glyoxylic acid,  $\text{CHO.CO}_2\text{H}$ , will receive attention under the uric acid derivatives. At this point we will yet mention those of carbonic acid: allophanic acid, biuret and carbonyl diurea.

**Allophanic Acid**,  $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \diagdown \\ \text{NH.CO}_2\text{H} \end{smallmatrix}$ , is not known in a free state. Its esters are formed when chlorcarbonic esters act upon urea:—



or by leading cyanic acid vapors into the anhydrous alcohols:—

$2\text{CO:NH} + \text{C}_2\text{H}_5.\text{OH} = \text{NH}_2.\text{CO.NH.CO}_2\text{C}_2\text{H}_5$ . At first carbamic acid esters are produced (p. 301); these combine with a second molecule of cyanic acid and yield allophanic esters. They are crystalline, difficultly soluble in water, and when heated split up into alcohols, ammonia and cyanuric acid. The allophanates are obtained from them by means of the alkalis or baryta water. These react alkaline and are decomposed by carbonic acid. On attempting to free the acid by means of mineral acids, it at once breaks up into  $\text{CO}_2$  and urea.

*Ethyl Allophanic Ester*,  $\text{NH}_2.\text{CO.NH.CO}_2\text{C}_2\text{H}_5$ , is obtained when hydrochloric acid acts upon a solution of potassium isocyanate dissolved in alcohol. Shining needles, melting at  $190\text{--}191^{\circ}$ . The *propyl ester* melts at  $155^{\circ}$ .

**Allophanamide**,  $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \diagdown \\ \text{NH.CO.NH}_2 \end{smallmatrix}$ , **Biuret**, is formed on heating the allophanic esters with ammonia to  $100^{\circ}$ , or urea to  $150\text{--}160^{\circ}$ :—



It is readily soluble in alcohol and ether, and crystallizes with 1 molecule  $\text{H}_2\text{O}$ , in the form of warts and needles. When anhydrous biuret melts at  $190^{\circ}$ , it further decomposes into  $\text{NH}_3$  and cyanuric acid. The aqueous solution, containing  $\text{KOH}$ , is colored a violet red by copper sulphate. Heated in a current of  $\text{HCl}$ , biuret decomposes into  $\text{NH}_3$ ,  $\text{CO}_2$ , cyanuric acid, urea and guanidine.

**Carbonyl Diurea**,  $\text{C}_3\text{H}_6\text{N}_4\text{O}_3$ , is formed on heating urea with  $\text{COCl}_2$  to  $100^{\circ}$ :—



It is a crystalline powder, not readily dissolved by water. Heat converts it into  $\text{NH}_3$  and cyanuric acid.

**Thio-urea**, **Sulphocarbamide**,  $\text{CS} \begin{smallmatrix} \text{NH}_2^* \\ \diagdown \\ \text{NH}_2 \end{smallmatrix}$ . It is obtained

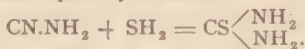
\* The hypothetical isothio-urea or imido-thiocarbamic acid,  $\text{HN} = \text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagdown \\ \text{SH} \end{smallmatrix}$ , is isomeric with thio-urea. It is, however, only known in its derivatives (p. 312 and phenyl-isothiurea).



by heating ammonium thiocyanate to  $170^{\circ}$ , when a transposition, analogous to that occurring in the formation of urea, takes place (p. 303):—



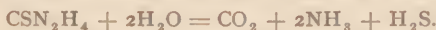
and by the action of  $\text{H}_2\text{S}$  (in presence of a little ammonia), or ammonium thiocyanate upon cyanamide:—



*Preparation.*—Heat dried ammonium thiocyanate to  $180^{\circ}$  for several hours. The mass is then treated with an equal weight of hot water and the filtered solution allowed to crystallize (*Ann.*, 179, 113).

Sulphocarbamide crystallizes in fine, silky needles, or in thick, rhombic prisms, which dissolve easily in water and alcohol, but with difficulty in ether; they possess a bitter taste and have a neutral reaction.

They melt at  $149^{\circ}$  and decompose at higher temperatures. When sulphocarbamide is heated with  $\text{H}_2\text{O}$  to  $140^{\circ}$  it again becomes ammonium thiocyanate. If boiled with alkalis, hydrochloric acid or sulphuric acid, it decomposes according to the equation:—

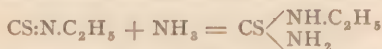


Nitrous acid eliminates nitrogen. Silver, mercury, or lead oxide and water will convert it, at ordinary temperatures, into cyanamide,  $\text{CN}_2\text{H}_2$ ; and on boiling into dicyandiamide (p. 248).

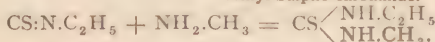
Thio-urea combines with 1 equivalent of acid to form salts. The *nitrate*,  $\text{CSN}_2\text{H}_4.\text{HNO}_3$ , occurs in large crystals. Auric chloride and platinic chloride throw down red colored double chlorides from the concentrated solution. Silver nitrate precipitates,  $(\text{CSN}_2\text{H}_4)_2.\text{Ag}_2\text{O} + 4\text{H}_2\text{O}$ , and mercuric nitrate,  $(\text{CSN}_2\text{H}_4)_2.3\text{HgO} + 3\text{H}_2\text{O}$  (see *Ber.*, 17, 297).

*Compound Sulphocarbamides*, in which hydrogen is replaced by alcohol radicals, are formed:—

(1) On heating the mustard oils (p. 241) with amine bases:—

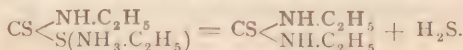


Ethyl Sulpho-carbamide.

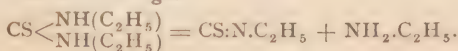


Ethyl-Methyl Sulphocarbamide.

(2) By heating the amide salts of the alkyl dithiocarbamic acids (p. 302):—



The sulphocarbamides regenerate amines and mustard oils by distillation with  $\text{P}_2\text{O}_5$ , or when heated in  $\text{HCl}$  gas:—

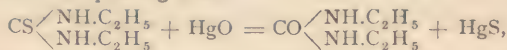


**Ethyl Sulphocarbamide**,  $\text{CS} \begin{smallmatrix} \text{NH.C}_2\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$ , crystallizes in needles, melting at  $106^\circ$ .

**Diethyl Sulphocarbamide**,  $\text{CS} \begin{smallmatrix} \text{NH.C}_2\text{H}_5 \\ \text{NH.C}_2\text{H}_5 \end{smallmatrix}$ , consists of large crystals, not very readily soluble in water. It melts at  $77^\circ$ .

**Methyl Ethyl Sulphocarbamide**,  $\text{CS} \begin{smallmatrix} \text{NH.CH}_3 \\ \text{NH.C}_2\text{H}_5 \end{smallmatrix}$ , is derived from ethyl mustard oil and methylamine. It melts at  $54^\circ$ .

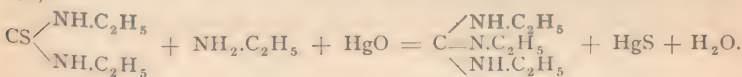
The sulphur in the alkylic sulphocarbamides may be replaced by oxygen if these compounds are boiled with water and  $\text{HgO}$ . Those that contain two alkyl groups yield the corresponding ureas:—



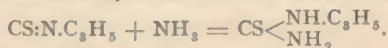
whereas the mono-derivatives pass into alkylic cyanamides (and melamines) after parting with  $\text{SH}_2$  (p. 248):—



On warming the dialkylic sulphocarbamides with mercuric oxide and amines, oxygen is exchanged for the imid-group and we get guanidine derivatives (p. 250):—



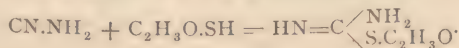
**Allyl Sulphocarbamide**,  $\text{CS} \begin{smallmatrix} \text{NH.C}_3\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$ , **Thio-sinamine**, is formed by the union of allyl mustard oil with ammonia:—



It forms shining prisms, with bitter taste, and melts at  $74^\circ$ . It decomposes at higher temperatures. It is readily soluble in water, alcohol and ether; combines with one equivalent of acid, and affords salts with acid reaction. Water decomposes them. Allyl cyanamide and triallyl-melamine are produced on boiling with mercuric oxide or lead hydroxide (p. 248):—

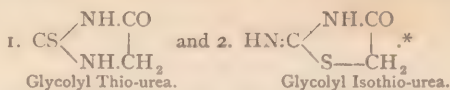
Acetyl sulphocarbamide and Thiohydantoïn are considered as *acid derivatives* of sulphocarbamide:—

**Acetyl Sulphocarbamide**,  $\text{CS} \begin{smallmatrix} \text{NH}_2 \\ \text{NH.C}_2\text{H}_3\text{O} \end{smallmatrix}$ , or  $\text{HN}=\text{C} \begin{smallmatrix} \text{NH}_2 \\ \text{S.C}_2\text{H}_3\text{O} \end{smallmatrix}$ , is obtained from thio-urea by heating it with acetic anhydride. Its formation from cyanamide (carbodiimide, p. 247) and thio-acetic acid argues for the second formula:—



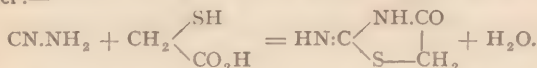
It crystallizes from hot water in prisms; these melt at  $165^\circ$ .

The so-called **Thio- or Sulpho-hydantoïn**,  $C_3H_4N_2SO$ , is not constituted according to the formula 1, corresponding to that of hydantoïn (p. 307), but according to 2:—



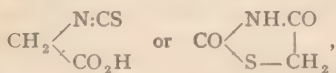
The grouping (*Ann.*, 207, 121) in this instance is analogous to that shown by the isothio-amides (p. 210) and the phenyl isothiourethanes (p. 302).

Sulphohydantoïn is obtained when chloracetic acid and its anhydride act on sulphocarbamide; or (analogous to the formation of acetylsulphocarbamide) by evaporating an aqueous solution of cyanamide and thioglycollic acid (p. 278), when the sulphohydantoïc acid (see below) produced at first, parts with a molecule of water:—



Sulphohydantoïn crystallizes from hot water in long needles, and decomposes near  $200^\circ$ . When boiled with baryta water it splits into thioglycollic acid and dicyandiamide. Unlike the thio-ureas, it is not desulphurized when boiled with lead oxide or mercuric oxide and water.

Boiling acids convert it into *mustard-oil acetic acid*, with elimination of  $\text{NH}_3$ :



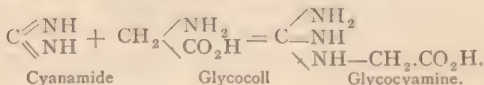
(*Ann.*, 207, 131).

**Sulphohydantoïc Acid**,  $C_3H_6N_2SO_2 = \text{HN:C} \begin{array}{l} \swarrow \text{NH}_2 \\ \searrow \text{S.CH}_2.\text{CO}_2\text{H} \end{array}$ , is obtained by heating sulphocarbamide with sodium chloracetic acid. It is a crystalline compound, not very soluble in water. It resembles the amido-acids in having a neutral reaction, but dissolves in alkalis and acids with production of salts. When heated with acids it reverts to thiohydantoïn.

## GUANIDINE DERIVATIVES.

Guanidine, like urea, is capable of yielding acid derivatives (p. 252), but few of them, however, are known. Creatine and creatinine, compounds of great significance physiologically, belong in this class and are derived from glycocyamine.

**Glycocyamine**,  $C_3H_7N_3O_2$ , guanidoacetic acid, is obtained by the direct union of glycolcoll with cyanamide:—



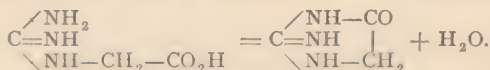
On mixing the aqueous solutions it deposits after a time in granular crystals. It is soluble in 120 parts cold water and rather

\* Real sulphohydantoïns (of the formula 1) have been prepared in the benzene series (see phenyl sulphhydantoïn and *Ber.*, 17, 425).

readily in hot water; while it is insoluble in alcohol and ether. With acids and bases it affords crystalline compounds. When boiled with water and lead peroxide, or with dilute sulphuric acid, it falls into guanidine, oxalic acid and carbon dioxide.

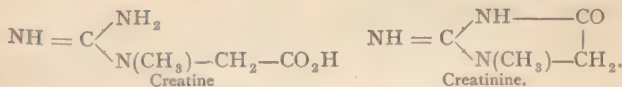
**$\beta$ -Guanidopropionic Acid**,  $C_4H_9N_3O_2$  (alacreatine,  $CN_3H_4 \cdot CH_2 \cdot CH_2 \cdot CO_2H$ ), is homologous with the preceding, and is obtained in a similar manner from cyanamide and  $\beta$ -amidopropionic acid. It melts at  $205^\circ$ . Isomeric  $\alpha$ -guanidopropionic acid melts at  $180^\circ$ .

**Glycocyamidine**,  $C_3H_5N_3O$ , glycolyl guanidine, bears the same relation to glycocyamine as hydantoic acid (p. 308). Its hydrochloride is produced when glycocyamine hydrochloride is heated to  $160^\circ$ :—

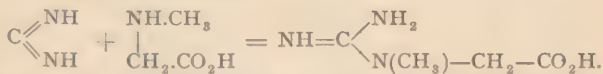


The free base crystallizes in deliquescent laminæ, having an alkaline reaction.  $\text{PtCl}_4$  precipitates its hydrochloride.

The methyl derivatives of glycocyamine and glycocyamidine are:—



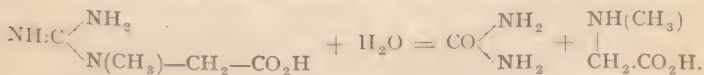
**Creatine**,  $C_4H_9N_3O_2$ , methyl glycoxyamine, occurs in the animal organism, especially in the juice of muscles. It may be artificially prepared, like glycoxyamine, by the union of sarcosine (methyl glycocoll) with cyanamide:—



To obtain creatine, exhaust finely divided flesh with cold water, boil the solution to coagulate the albumen, precipitate the phosphoric acid in the filtrate with baryta water and evaporate the liquid, then let it crystallize.

Creatine crystallizes with one molecule of water in glistening prisms. Heated to  $100^{\circ}$  they sustain a loss of water. It reacts neutral, has a faintly bitter taste and dissolves rather readily in boiling water; it is very difficultly soluble in alcohol, and affords crystalline salts with one equivalent of acid.

With boiling acids creatine loses water and becomes creatinine (see above), and with baryta water it falls into urea and sarcosine:



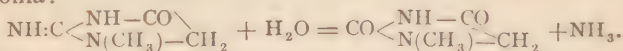
Ammonia is liberated at the same time and methyl hydantoin (p. 308) formed. When its aqueous solution is heated with mercuric



oxide, creatine becomes oxalic acid and methyl guanidine. Ammonia and methylamine are disengaged when it is ignited with soda-lime.

**Creatinine**,  $C_4H_7N_3O$ , methyl glycoyamidine, occurs constantly in urine (about 0.25 per cent.), and is readily obtained from creatine by evaporating its aqueous solution, especially when acids are present. It crystallizes in rhombic prisms and is much more soluble than creatine, in water and alcohol. It is a strong base which can expel ammonia from ammonium salts and yields well crystallized salts with acids. Its compound with zinc chloride,  $(C_4H_7N_3O)_2 \cdot ZnCl_2$ , is particularly characteristic. Zinc chloride precipitates it from creatinine solutions as a difficultly soluble, crystalline powder.

Bases cause creatinine to absorb water and become creatine again. Boiled with baryta water it decomposes into methyl hydantoin and ammonia:—



When boiled with mercuric oxide it breaks up like creatine into methyl-guanidine and oxalic acid.

When creatinine is heated with alcoholic ethyl iodide, the ammonium iodide of ethyl creatinine,  $C_4H_7(C_2H_5)_3N_3O \cdot I$ , is produced. Silver oxide converts this into the ammonium base,  $C_4H_7(C_2H_5)_3N_3O \cdot OH$ .

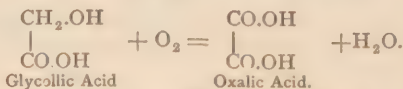
#### DIBASIC ACIDS, $C_nH_{2n-2}O_4$ .

Oxalic	Acid	$C_2H_2O_4 = (CO_2H)_2$
Malonic	"	$C_3H_4O_4 = CH_2(CO_2H)_2$
Succinic	Acids	$C_4H_6O_4 = C_2H_4(CO_2H)_2$
Pyrotartaric	"	$C_5H_8O_4 = C_3H_6(CO_2H)_2$
Adipic	Acid	$C_6H_{10}O_4 = C_4H_8(CO_2H)_2$ , etc.

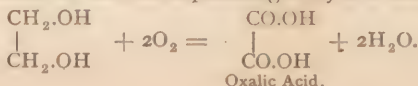
The acids of this series contain two carboxyl groups, hence are *dibasic*. They are produced according to methods analogous to those employed with the monobasic acids, by a repetition of the formation of the carboxyl group.

The most important general methods are:—

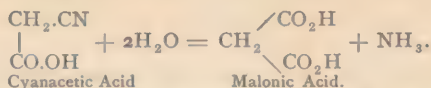
(1) By oxidation of oxy-fatty acids, in which OH is linked to  $CH_2$ :—



(2) By oxidation of the corresponding dihydric alcohols:—



(3) Conversion of monohalogen substituted fatty-acids into cyan derivatives, and boiling the latter with alkalis or acids (pp. 168 and 212):—

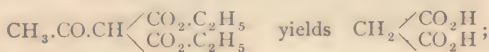


(4) Conversion of the halogen addition products of the alkylens,  $\text{C}_n\text{H}_{2n}$ , into cyanides and the saponification of the latter:—

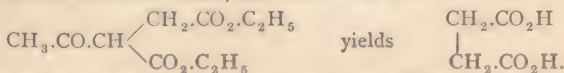


Only the halogen products having their halogens attached to two different carbon atoms can be converted into dicyanides.

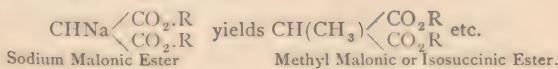
(5) A very general method for the synthesis of dibasic acids is founded upon the transposition of aceto-acetic esters. Acid residues are introduced into the latter and the products decomposed by concentrated alkali solutions (p. 222). Thus from aceto-malonic ester we get malonic acid:—



and from aceto-succinic ester, succinic acid:—



(6) In a perfectly similar manner, higher dibasic acids can be prepared from malonic esters,  $\text{CH}_2(\text{CO}_2\text{R})_2$ . An hydrogen atom of  $\text{CH}_2$  is replaced by sodium and then the alkyls introduced by means of the alkyl iodides:—



In these monoalkylic esters the second hydrogen atom can be replaced by sodium and alkyls:—



The free acids are obtained by saponifying the esters with alkalis.

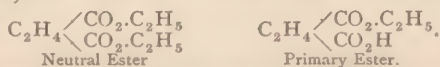
In performing these syntheses the malonic ester is mixed with the theoretical amount of sodium dissolved in absolute alcohol (10 volumes), the alkyl iodide added and heat applied until the alkaline reaction disappears. After expelling the excess of alcohol the ester is precipitated with water (in preparing the dialkyl derivatives 2 equivalents of sodium alcoholate and alkyl iodide are added. *Ann.*, 204, 129). Tri- and poly-carboxylic acids may likewise be obtained by the introduction of acid esters (by means of chloracetic ester, etc.—(p. 217 and *Ber.*, 15, 1109).

The dibasic acids are also formed on oxidizing the fatty acids  $C_nH_{2n}O_2$ , the acids of the oleic acid series, and the fats with nitric acid. Potassium permanganate oxidizes some hydrocarbons,  $C_nH_{2n}$ , to dibasic acids.

The acids of this series are solids, crystallizable, and generally volatile without decomposition. They are mostly soluble in water and have a strong acid reaction. The melting points of the normal dicarboxylic acids exhibit the same regularity observed with the fatty-acids (p. 172) *i. e.*, the members containing an even number of carbon atoms melt higher than those with an odd number (*Ber.* 10, 1286).

At higher temperatures those members which are capable of yielding anhydrides part with water and pass into such compounds, whereas, the others *having both carboxyl groups attached to one carbon atom*, decompose more or less readily into  $CO_2$  and mono-basic fatty-acids (p. 169). Thus from oxalic acid we get formic acid, from malonic acid,  $CH_2(CO_2H)_2$ , acetic acid, from isosuccinic acid,  $CH_3.CH(CO_2H)_2$ , propionic acid, etc.

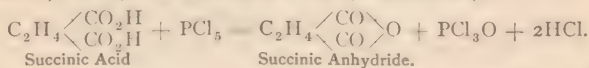
Having two carboxyls, the dibasic acids can form neutral and acid salts, likewise neutral and acid esters or ether-acids (similar to sulphuric acid):—



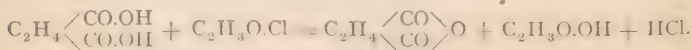
The best method to use in making the *neutral esters* is to dissolve the acid in alcohol, and while applying heat lead in a stream of hydrogen chloride gas; on adding water the ester is precipitated, and may then be purified either by distillation or crystallization.

See *Berichte*, 14, 2630, for the ester formation of dibasic acids (p. 204).

With the dibasic acids the *anhydride formation* takes place within *one* molecule, and leads to the formation of *inner* anhydrides; those resulting from the union of two molecules are not known (p. 274). The anhydrides are obtained by either heating the acids (see above), or by the action of  $PCl_5$  (1 molecule):—



In many cases the analogous action of chlorides of the fatty acids, *e. g.*, acetyl chloride, on the free acids or their silver salts, is better adapted to the preparation of anhydrides (*Ber.*, 10, 1881, and 13, 1844):—

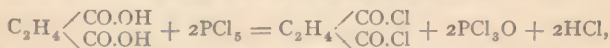


It is a singular fact that anhydrides cannot be prepared from oxalic acid,  $C_2O_4H_2$ , malonic acid,  $CH_2(CO_2H)_2$ , isosuccinic acid,

$\text{CH}_3\cdot\text{CH}(\text{CO}_2\text{H})_2$ , etc., whereas succinic acid, normal pyrotartaric acid, also maleïc and phthalic acids are capable of such formations. It seems, then, that anhydrides are only possible with dicarboxylic acids (p. 275) in which there is a chain of four or five carbon atoms.

The anhydrides of this series are perfectly analogous in properties and transpositions to those of the fatty acids; they slowly dissolve in water, more readily on heating, with regeneration of their acids.

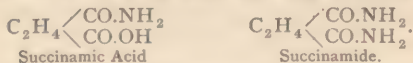
When 2 molecules of  $\text{PCl}_5$  are permitted to act on the dicarboxylic acids chloranhydrides of the acids are formed:—



which conduct themselves in all respects like monovalent acid chlorides.

The divalent residues joined to the two OH's are termed the *radicals* of the dicarboxylic acids, *e. g.*,  $\text{C}_2\text{O}_2$ , oxalyl,  $\text{CH}_2(\text{CO})_2$ , malonyl,  $\text{C}_2\text{H}_4(\text{CO})_2$ , succinyl.

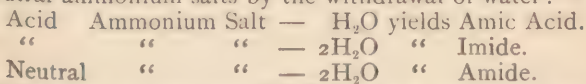
The *amides* are similar to those of the monobasic acids (p. 208). Both *acid amides* or *amic acids*, and the real *diamides* exist:—



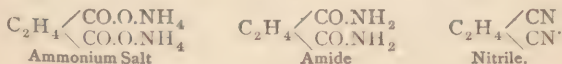
The *imides* are derived by substituting divalent acid radicals for two hydrogen atoms in one molecule of ammonia (*Ann.*, **215**, 172):—



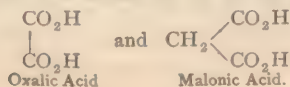
The amide compounds may also be derived from the primary and neutral ammonium salts by the withdrawal of water:—



By withdrawing 4 molecules of  $\text{H}_2\text{O}$  from the neutral salt we obtain the acid nitriles or cyanides of the divalent alcoholic radicals (p. 241):—

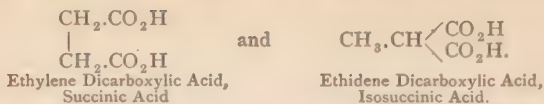


The possible cases of isomerism correspond with those of the  $\text{C}_n\text{H}_{2n}$  hydrocarbon groups; the two  $\text{COOH}$  groups may be attached to two different carbon atoms or to a single carbon atom. Isomerides of the first two members of the series—



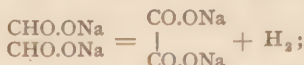


are not possible. For the third member two structural cases exist :—

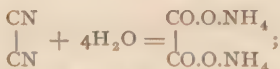


There are four possible isomerides with the formula  $\text{C}_3\text{H}_6\begin{array}{l} \swarrow \text{CO}_2\text{H} \\ \searrow \text{CO}_2\text{H} \end{array}$ , etc. Many acids are named from malonic acid; this accords with their synthesis and is quite practicable (p. 315).

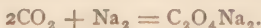
1. **Oxalic Acid**,  $\text{C}_2\text{O}_4\text{H}_2$  (*Acidum oxalicum*), occurs in many plants, chiefly as potassium salt in the different varieties of *Oxalis* and *Rumex*. The calcium salt is often found crystallized in plant cells; it constitutes the chief ingredient of certain calculi. The acid may be prepared artificially by oxidizing many carbon compounds with nitric acid, or by fusing them with alkalis. It is formed synthetically by rapidly heating sodium formate above  $440^\circ$  :—



by oxidizing formic acid with nitric acid (*Ber.*, 17, 9); by adding water to cyanogen :—



and by conducting carbon dioxide over metallic sodium heated to  $350$ – $360^\circ$  :—



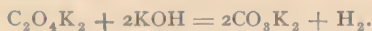
Formerly, the acid was obtained from the different oxalis species or by oxidizing sugar with nitric acid. At present it is prepared on an immense scale by fusing sawdust with a mixture of KOH and NaOH (equal parts) in iron pans and maintaining a temperature of  $200$ – $220^\circ$ . The brown fusion is extracted with water and boiled with milk of lime. The separated calcium salt is decomposed with sulphuric acid and the filtrate evaporated to crystallization.

The ease with which sodium oxalate is produced from sodium formate (above), and the latter from CO and NaOH (p. 173) would make it appear possible to obtain the acid on a commercial scale by these reactions (*Ber.*, 15, 1508).

Oxalic acid with the formula,  $\text{C}_2\text{H}_2\text{O}_4 + 2\text{H}_2\text{O} = \text{C}_2(\text{OH})_6$ , crystallizes in fine, transparent, monoclinic prisms, which effloresce at  $20^\circ$  in dry air and fall to a white powder. It is soluble in 9 parts of water of ordinary temperature. When carefully heated to  $150^\circ$  the anhydrous acid sublimes undecomposed; rapidly heated it decomposes into formic acid and carbon dioxide :—



Oxalic acid decomposes into carbonate and hydrogen by fusion with alkalis or soda-lime (p. 174):—



Heated with concentrated sulphuric acid it yields carbon monoxide, dioxide and water:—



Nascent hydrogen (Zn and  $\text{H}_2\text{SO}_4$ ) converts it into glycollic acid.

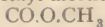
The oxalates, excepting those with the alkali metals, are almost insoluble in water.

The *neutral potassium salt*,  $\text{C}_2\text{O}_4\text{K}_2 + \text{H}_2\text{O}$ , is very soluble in water, and parts with its water of crystallization at  $180^\circ$ . The acid salt,  $\text{C}_2\text{O}_4\text{HK}$ , is more difficultly soluble and occurs in the juices of plants (of *Oxalis* and *Rumex*). *Potassium quadroxalate*,  $\text{C}_2\text{O}_4\text{KH}$ ,  $\text{C}_2\text{O}_4\text{H}_2 + 2\text{H}_2\text{O}$ , forms triclinic crystals, soluble in 20 parts  $\text{H}_2\text{O}$  at  $20^\circ$ . Commercial salt of sorrel consists generally of a mixture of the acid and the super-salt.

*Neutral Ammonium Oxalate*,  $\text{C}_2\text{O}_4(\text{NH}_4)_2 + \text{H}_2\text{O}$ , consists of shining, rhombic prisms, and is easily soluble in water. When heated it becomes oxamide, which further decomposes into  $\text{C}_2\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{NH}_3$ . *Acid ammonium oxalate*,  $\text{C}_2\text{O}_4\text{H}(\text{NH}_4)$ , yields oxamic acid on heating. The *calcium oxalate*,  $\text{C}_2\text{O}_4\text{Ca} + \text{H}_2\text{O}$ , is found in a crystalline state in plant cells; it is precipitated as a white crystalline powder (quadratic octahedra) on the addition of an oxalate to a warm solution of a calcium salt. (A salt with  $3\text{H}_2\text{O}$  separates from very dilute and cold solutions.) Calcium oxalate is insoluble in water and acetic acid, but is dissolved by the mineral acids. It parts with its water of crystallization at  $200^\circ$ . The *silver salt*,  $\text{C}_2\text{O}_4\text{Ag}_2$ , explodes when quickly heated.

## ESTERS OF OXALIC ACID.

**Oxalic Methyl Ester**,  $\text{C}_2\text{O}_2(\text{CH}_3)_2$ , is obtained by distilling oxalic acid (1 part) or potassium oxalate (2 parts) with methyl alcohol (1 part) and sulphuric acid (1 part); or by boiling anhydrous oxalic acid with methyl alcohol. It forms large, rhombic plates, which are easily soluble in water and alcohol; possesses an aromatic odor, melts at  $51^\circ$  and distils at  $163^\circ$ . Water, especially when boiling, decomposes it into oxalic acid and methyl alcohol.



The *acid ester* (methyl oxalic acid),  $\text{CO.OH}$ , is very unstable, and is found in

the mother-liquor from the neutral ester.

**Oxalic Ethyl Ester**,  $\text{C}_2\text{H}_2(\text{O.C}_2\text{H}_5)_2$ , is an aromatic-smelling liquid, of sp. gr. 1.0793 at  $20^\circ$  and boils at  $186^\circ$ . It is difficultly soluble in water, and is gradually decomposed by it into oxalic acid and ethyl alcohol. It is produced by distilling equal parts of salt of sorrel, alcohol and sulphuric acid. The following method affords it more readily. Anhydrous oxalic acid (3 parts) is dissolved on the water bath, in absolute alcohol (2 parts), and the solution then introduced into a tubulated retort and heated to  $100^\circ$ . Gradually raising the temperature to  $130^\circ$ , the vapor of 2 parts absolute alcohol is conducted into the liquid; water and alcohol distil off. The oxalic ester is separated from the residue by fractional distillation.

It forms oxamide and alcohol when shaken with aqueous ammonia; dry ammonia converts it into oxamic ester. *Potassium ethyl oxalate*,  $\text{C}_2\text{O}_2 \begin{smallmatrix} \diagup \text{O.C}_2\text{H}_5 \\ \diagdown \text{OK} \end{smallmatrix}$ , mixed with  $\text{C}_2\text{O}_4\text{K}_2$ , is precipitated by adding alcoholic potash to a solution of

oxalic ester. The same salt is formed when monochloroacetic ester is heated with  $\text{KNO}_2$ . It is a crystalline powder, which decomposes above  $140^\circ$ . Free *ethyl oxalic acid* is obtained by heating anhydrous oxalic acid with absolute alcohol, and distils undecomposed at  $117^\circ$  under 15 mm. pressure. Distilled under ordinary atmospheric pressure it decomposes into  $\text{CO}_2$ , formic ester and oxalic ester.

$\text{POCl}_3$  converts potassium ethyl oxalate into **chloroxalic ester**,  $\text{C}_2\text{O}_2 \begin{smallmatrix} \diagup \text{Cl} \\ \diagdown \text{O.C}_2\text{H}_5 \end{smallmatrix}$ . A better method is to heat oxalic ester with  $\text{PCl}_5$  until no more ethyl chloride is disengaged:—



When separated from the  $\text{POCl}_3$  by fractional distillation, ethyl oxalyl chloride is a pungent-smelling liquid, boiling at  $131.5^\circ$ . It fumes strongly in the air and rapidly decomposes into oxalic acid,  $\text{HCl}$  and alcohol. It reacts very energetically with alcohol and affords neutral esters. By further heating with  $\text{PCl}_5$ , it is slowly changed to trichloroacetic ester.

The **Isoamyl Ester**,  $\text{C}_2\text{O}_2(\text{O.C}_5\text{H}_{11})_2$ , is obtained by heating amyl alcohol with oxalic acid. It is a thick oil which boils at  $262^\circ$ , and smells like bedbugs.

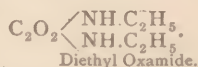
$\text{PCl}_5$  converts it into *amyl oxalyl chloride*,  $\text{C}_2\text{O}_2 \begin{smallmatrix} \diagup \text{Cl} \\ \diagdown \text{O.C}_5\text{H}_{11} \end{smallmatrix}$ , an oil which partly decomposes on the application of heat (*Ber.*, 14, 1750).

The **Allyl Ester**,  $\text{C}_2\text{O}_2(\text{O.C}_3\text{H}_5)_2$ , obtained by the action of allyl iodide on silver oxalate, boils at  $206\text{--}207^\circ$ , and has a specific gravity of 1.055°.

## AMIDES OF OXALIC ACID.

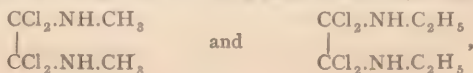
**Oxamide**,  $\text{C}_2\text{O}_2(\text{NH}_2)_2$ , separates as a white, crystalline powder, when neutral oxalic ester is shaken with aqueous ammonia. It is insoluble in water and alcohol. It is also formed when water and a trace of aldehyde act on cyanogen,  $\text{C}_2\text{N}_2$ , or by the direct union of hydrocyanic acid and hydrogen peroxide ( $2\text{CNH} + \text{H}_2\text{O}_2 = \text{C}_2\text{O}_2\text{N}_2\text{H}_4$ ). Oxamide is partially sublimed when heated, the greater part, however, being decomposed. When heated to  $200^\circ$  with water, it is converted into ammonium oxalate.

The substituted oxamides containing alcohol radicals are produced by the action of the primary amines upon the oxalyl esters, *e. g.*:—



These compounds are more soluble in hot water and alcohol than oxamide, and distil without decomposition. The first melts at  $210^\circ$ . The alkalis break them up into oxalic acid and amines.

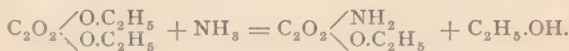
When two molecules of  $\text{PCl}_5$  act upon dimethyl or diethyl oxamide the oxygen atoms are replaced by  $\text{Cl}_2$ . The resulting amid-chlorides (*p.* 269)—



readily part with three molecules of HCl and yield chlorinated bases: *chloroxal-methylin*,  $C_4H_5ClN_2$ , and *chloroxalethylin*,  $C_6H_9ClN_2$ . Both are very alkaline liquids, soluble in water; the first boils at  $205^\circ$ , the second at  $217-218^\circ$ . On heating them with hydriodic acid and amorphous phosphorus we get bases not containing chlorine; *Oxalmethylin*,  $C_4H_6N_2$ , and *Oxalethylin*,  $C_6H_{10}N_2$ ; the first is identical with methyl glyoxalin, the second with ethyl glyoxalethylin (p. 280).

**Oxamic Acid**,  $C_2O_2 \begin{smallmatrix} \diagup NH_2 \\ \diagdown OH \end{smallmatrix}$ , is obtained from its ammonium salt, which is produced by heating acid ammonium oxalate, or by boiling oxamide with ammonia. It is a crystalline powder, difficultly soluble in cold water, and melts at  $173^\circ$ . It is monobasic and affords crystalline salts. It passes into acid ammonium oxalate when heated with water.

Its *esters* result from the action of alcoholic or dry ammonia upon the esters of oxalic acid:—



*Ethyl Oxamic Ester* (Oxamethane),  $C_2O_2 \begin{smallmatrix} \diagup NH_2 \\ \diagdown O.C_2H_5 \end{smallmatrix}$ , consists of shining, fatty-feeling leaflets. It melts at  $114-115^\circ$  and boils at  $205^\circ$ .  $PCl_5$  converts it into the *amid-chloride*,  $CCl_2(NH_2).CO.O.C_2H_5$  (see above), a crystalline compound, which reverts to oxamethane, when exposed to moist air. HCl separates when heat is applied and the product is cyancarbonic ester,  $CN.CO.O.C_2H_5$ . Isomeric bodies, alkylic oxamic acids, are obtained by heating salts of the primary amines of oxalic acid. Ethyloxamic acid,  $C_2O_2 \begin{smallmatrix} \diagup NH.C_2H_5 \\ \diagdown OH \end{smallmatrix}$ , crystallizes in six-sided plates and melts at  $120^\circ$ .

*Ethyl Dietho-oxamic Ester*,  $C_2O_2 \begin{smallmatrix} \diagup N(C_2H_5)_2 \\ \diagdown O.C_2H_5 \end{smallmatrix}$  (Diethyloxamethane), boils at  $254^\circ$  and is produced by the action of diethylamine upon oxalic esters. It regenerates diethylamine on distilling with potash. A method for separating the amines (p. 123) is based on this behavior.

Cyanogen is the nitrile of oxalic acid (p. 226).

The *oximido-ether* is produced when HCl acts upon cyanogen in alcoholic solution:—



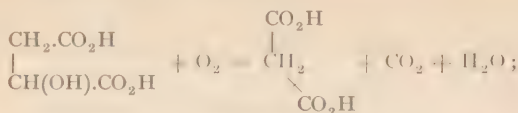
This is analogous to the formation of the imido-ethers (p. 248) from nitriles.

Alcoholic ammonia converts the product into *oxamidine*,  $C(NH).NH_2$   
 $\begin{array}{c} | \\ C(NH).NH_2 \end{array}$  (Ber., 16, 1655).

(2) **Malonic Acid**,  $C_3H_4O_4 = CH_2(COOH)_2$ , occurs in the deposit found in the vacuum pans employed in the beet sugar



manufacture. It is obtained by the oxidation of malic acid (and hydracrylic acid) with chromic acid:—



by the decomposition of malonyl urea (barbituric acid, see this) with alkalis, and by the oxidation of propylene and allylene with  $\text{KMnO}_4$ . It may be prepared, too, by boiling cyanacetic acid (p. 212) with alkalis or acids:—



*Preparation.*—100 grams of chloracetic acid, dissolved in 200 grams water, are neutralized with sodium carbonate (110 grams), and to this 75 grams of pure, pulverized potassium cyanide are added, and the whole carefully heated, after solution, upon a water-bath. The cyanide produced is saponified either by concentrated hydrochloric acid or potassium hydrate (*Ber.*, 13, 1358, and *Ann.*, 204, 125). To obtain the malonic ester directly, evaporate the cyanide solution, cover the residue with absolute alcohol and lead  $\text{HCl}$  gas into it (*Ann.*, 218, 131).

Malonic acid crystallizes in large tables or laminæ. It is easily soluble in water, alcohol and ether, and melts at  $132^\circ$ . At highest temperatures it decomposes into acetic acid and carbon dioxide. The ethyl ester is similarly broken up into  $\text{CO}_2$  and acetic ester when it is heated with water to  $150^\circ$ . Bromine in aqueous solution converts it into tribromacetic acid and  $\text{CO}_2$ . Its *barium salt*,  $(\text{C}_3\text{H}_2\text{O}_4)_2\text{Ba} + 2\text{H}_2\text{O}$ , forms silky, shining needles. The *calcium salt*,  $(\text{C}_3\text{H}_2\text{O}_4)_2\text{Ca} + 3\frac{1}{2}\text{H}_2\text{O}$ , is very difficultly soluble in cold water, hence is precipitated by calcium chloride from neutral solutions. Silver nitrate precipitates the *silver salt*,  $\text{C}_3\text{H}_2\text{Ag}_2\text{O}_4$ , as a white, crystalline compound.

The *malonic esters* are obtained by dissolving the acid in alcohol, and conducting  $\text{HCl}$  into the solution (see above).

The *methyl ester*,  $\text{CH}_2(\text{CO}_2\text{CH}_3)_2$ , boils at  $175\text{--}180^\circ$ . The *ethyl ester* boils at  $195^\circ$ ; its specific gravity at  $18^\circ$  is 1.068.

The amide of malonic acid  $(\text{CH}_2(\text{CO}.\text{NH}_2)_2)$  melts at  $170^\circ$  (*Ber.*, 17, 133).

As in the aceto-acetic esters, so in the malonic esters, the hydrogen of the methylene group ( $\text{CH}_2$ ) can be replaced by alkali metals (p. 315). When nitrous acid is conducted into the solution of the sodium compound of the ethyl ester, we get *Isonitrosomalonic ester*,  $\text{C}(\text{N.OH})(\text{CO}_2\text{C}_2\text{H}_5)_2$ . This is a yellow oil which decomposes when heated. Its specific gravity at  $15^\circ$  is 1.149. Saponification with alkalis liberates *isonitrosomalonic acid*,  $\text{C}(\text{N.OH})(\text{CO}_2\text{H})_2$ . This is also formed by the action of hydroxylamine (*Ber.*, 16, 608, 1621) upon violuric acid (see this) and mesoxalic acid,  $\text{CO}(\text{CO}_2\text{H})_2$ . It is easily soluble in water, crystallizes in shining needles, and melts near  $126^\circ$ , decomposing at the same time into  $\text{CNH}$ ,  $\text{CO}_2$  and water. **Amidomalonic Acid**,  $\text{CH}(\text{NH}_2).(\text{CO}_2\text{H})_2$

$\text{H})_2$ , is obtained from it by reduction with sodium amalgam. This new acid is readily dissolved by water, and when warmed passes into glycocoll,  $\text{CH}_2(\text{NH}_2)$ .  $\text{CO}_2\text{H}$  and  $\text{CO}_2$ . The amide of amidomalonic acid is obtained from chloromalonic ester (*Ber.*, 15, 607).

**Chloromalonic Ester**,  $\text{CHCl}(\text{CO}_2\text{C}_2\text{H}_5)_2$ , is obtained by conducting chlorine into warm malonic ethylate. It boils at  $222^\circ$ . When saponified with excess of caustic alkalis it yields oxymalonic acid (tartronic acid),  $\text{CH}(\text{OH})(\text{CO}_2\text{H})_2$ . The addition of one molecule of sodium ethylate to its solution produces at first sodium chloromalonic ester,  $\text{CNaCl}(\text{CO}_2\text{R})_2$ . The alkylogens convert this into chlorinated alkyl malonic esters (*Ber.*, 13, 2159). The latter yield higher oxydicarboxylic acids,  $\text{R}.\text{C}(\text{OH})(\text{CO}_2\text{H})_2$  (*Ann.*, 209, 232), when saponified with excess of caustic alkalis.

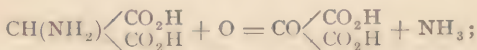
Two molecules of sodium alcoholate convert it into the sodium salt of *chloromalonic acid*, which crystallizes in shining prisms that melt at  $133^\circ$ , and at  $180^\circ$  decompose into  $\text{CO}_2$  and monochloroacetic acid (*Ber.*, 15, 605).

**Monobrom-malonic Acid**,  $\text{CHBr}(\text{CO}_2\text{H})_2$ , is produced in slight quantity when malonic acid is treated with bromine. It consists of deliquescent needles. Silver oxide converts it into oxymalonic acid (tartronic acid).

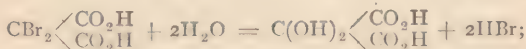
**Dibrom-malonic Acid**,  $\text{CBr}_2(\text{CO}_2\text{H})_2$ , is formed when bromine (dissolved in chloroform) is allowed to act upon malonic acid. Deliquescent needles, which melt at  $126^\circ$  and then further decompose. Heated with baryta water it changes to dioxymalonic acid (mesoxalic acid).

**Cyanmalonic Ester**,  $\text{CH}(\text{CN})(\text{CO}_2\text{R})_2$ , results from the action of cyanogen chloride upon sodium malonic ester. It is a pungent-smelling liquid, which boils with decomposition in a vacuum. It has a very acid reaction, and decomposes the alkaline carbonates, forming salts, like  $\text{CNa}(\text{CN})(\text{CO}_2\text{R})_2$  (*Ber.*, 15, 2244).

**Mesoxalic Acid**,  $\text{C}_3\text{H}_2\text{O}_5 = \text{CO}(\text{CO}_2\text{H})_2$  or  $\text{C}_3\text{H}_4\text{O}_6 = \text{C}(\text{OH})_2(\text{CO}_2\text{H})_2$ , dioxymalonic acid, is formed from amidomalonic acid by oxidation with iodine in an aqueous solution of potassium iodide:—



from dibrom-malonic acid by boiling with baryta water or silver oxide:—



and by boiling alloxan (mesoxalyl urea) with baryta water.

**Preparation.**—Add barium alloxanate (5 gr.) to water (1 litre) of  $80^\circ$ , then quickly heat to boiling (5–10 minutes) and filter. As the solution cools, barium mesoxalate will separate in the form of a fine, crystalline powder. It is decomposed with an equivalent quantity of sulphuric acid, the barium sulphate removed by filtration and the solution concentrated at a temperature of  $40\text{--}50^\circ$ , until the remaining mesoxalic acid solidifies in a crystalline mass.

Mesoxalic acid crystallizes in deliquescent prisms containing 1 molecule  $\text{H}_2\text{O}$ ; it melts at  $115^\circ$  without loss of water, and at higher temperatures decomposes into  $\text{CO}_2$  and glyoxylic acid,  $\text{CHO}.\text{CO}_2\text{H}$ . It breaks up into CO and oxalic acid by the evaporation of its aqueous solution.

As mesoxalic acid contains 1 molecule of water intimately combined, and as all its salts dried at  $110^{\circ}$  contain 1 molecule  $H_2O$ , it is considered a dihydroxyl derivative—dioxymalonic acid,  $C(OH)_2 \cdot (CO_2H)_2$ . Here, as in the case of glyoxylic acid, we observe an intimate union of two OH groups to 1 carbon atom, already combined with negative  $CO_2H$  groups (p. 253). Again, mesoxalic acid deports itself like a ketonic acid (p. 214), inasmuch as, with a loss of water, it unites with primary alkaline sulphites, and when acted upon by sodium amalgam in an aqueous solution of  $90^{\circ}$ , it is changed to tartronic acid :—

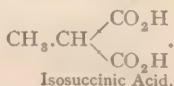
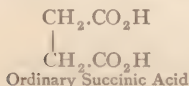


It combines with hydroxylamine to isonitrosomalonic acid (p. 322).

Barium mesoxalate,  $C(OH)_2 \begin{matrix} \diagup CO_2 \\ \diagdown CO_2 \end{matrix} Ba$ , and calcium mesoxalate are crystalline powders, not very soluble in water. The *ammonium salt*,  $C(OH)_2 \cdot (CO_2 \cdot NH_4)_2$ , obtained by evaporating a solution of the acid in ammonium carbonate, crystallizes in needles. The *silver salt*,  $C(OH)_2 \cdot (CO_2 Ag)_2$ , is a white amorphous powder, which blackens on exposure to the air, and when boiled with water affords mesoxalic acid, silver oxalate, silver and  $CO_2$ .

The *diethyl ester*,  $C(OH)_2 (CO_2 \cdot C_2H_5)_2$ , is obtained by the action of  $C_2H_5I$  upon the silver salt. It is an unstable oil. It affords a crystalline diamide,  $C(OH)_2 \cdot (CO \cdot NH_2)_2$ , with aqueous ammonia. Acetyl chloride converts it into the *diacetyl compound* (!)  $C(O \cdot C_2H_3O)_2 \begin{matrix} \diagup CO_2 \cdot C_2H_5 \\ \diagdown CO_2 \cdot C_2H_5 \end{matrix}$  (p. 156), which crystallizes in long needles, melting at  $145^{\circ}$ .

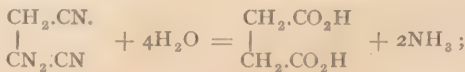
### 3. Succinic Acids, $C_4H_6O_4 = C_2H_4 \begin{matrix} \diagup CO_2H \\ \diagdown CO_2H \end{matrix}$



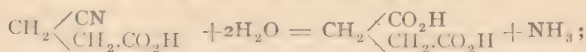
1. **Succinic Acid**, or ethylene dicarboxylic acid, occurs in amber, in some varieties of lignite, in resins, turpentine oils and in animal fluids. It is formed in the oxidation of fats with nitric acid, in the fermentation of calcium malate or ammonium tartrate and in the alcoholic fermentation of sugar.

It is synthetically prepared :—

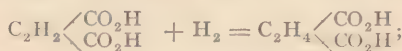
(1) By boiling ethylene cyanide (from ethylene bromide) (p. 257) with alkalis or acids :—



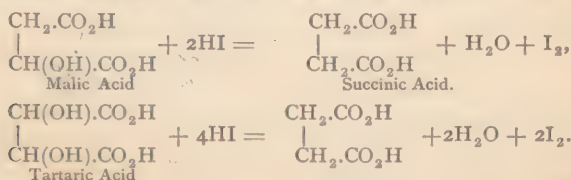
(2) By converting  $\beta$ -iodopropionic acid (p. 180) into cyanide and decomposing the latter with alkalis or acids:—



(3) By the action of nascent hydrogen upon fumaric and maleïc acids:—



(4) By reducing malic acid (oxysuccinic acid) and tartaric acid (dioxysuccinic acid) with hydriodic acid (p. 67):—



Malic acid undergoes a like reduction in the fermentation of its calcium salt.

(5) By the decomposition of aceto-succinic esters (p. 315).

*Preparation.*—Distil amber from an iron retort; evaporate the distillate and purify the residual, brown crystalline mass by crystallization from dilute nitric acid. The acid is easily prepared by letting calcium malate ferment. Water and rancid cheese are added to crude calcium malate and the mixture let stand at a temperature of 30–40° for several days. Subsequently the succinate of calcium, obtained in this manner, is decomposed with sulphuric acid, the gypsum filtered off and the filtrate evaporated to crystallization. Consult *Ber.*, 14, 214, upon the production of succinic acid by the fermentation of ammonium tartrate.

Succinic acid crystallizes in monoclinic prisms or plates, and has a faintly acid, disagreeable taste. It melts at 180° and distils at 235°, at the same time decomposing partly into water and succinic anhydride. At ordinary temperatures it dissolves in 20 parts of water. It is more difficultly soluble in alcohol. Ether will extract nearly all of the acid from its aqueous solution.

Uranium salts decompose aqueous succinic acid in sunlight into propionic acid and CO<sub>2</sub>. The galvanic current acts as indicated by the equation (p. 46):—



The salts with the alkali metals are readily soluble in water. The *potassium salt*, C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>K<sub>2</sub> + 3H<sub>2</sub>O, forms deliquescent needles. The *calcium salt*, C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>Ca, separates with 3 molecules H<sub>2</sub>O from a cold solution, but when deposited from a hot liquid it contains only 1H<sub>2</sub>O. It is difficultly soluble in water. When ammonium succinate is added to a solution containing a ferric salt, all the iron is precipitated as reddish-brown basic ferric succinate.



**Ethyl Succinic Ester**,  $C_2H_4(CO_2.C_2H_5)_2$ , is obtained in the action of hydrochloric acid upon an alcoholic solution of succinic acid. It is a thick oil, insoluble in water and boils at  $216^\circ$ .

Its specific gravity at  $0^\circ$  is 1.072. Sodium converts it into ethyl succino-succinate (p. 223).

**Succinic Anhydride** (succinyl oxide),  $C_2H_4\begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$ , is produced in the distillation of succinic acid, or more readily by heating it with 1 molecule of  $PCl_5$ ; further, by heating succinic acid with acetyl chloride (p. 316). It crystallizes in needles or prisms from alcohol or ether, melts at  $120^\circ$  and distils at  $250^\circ$ . When boiled with water it reverts to succinic acid.

Two molecules of  $PCl_5$  convert succinic acid into :—

**Succinyl Chloride**,  $C_2H_4\begin{smallmatrix} \diagup CO.Cl \\ \diagdown CO.Cl \end{smallmatrix}$ , an oil solidifying at  $0^\circ$  and boiling at  $190^\circ$ . By acting with sodium amalgam upon an ethereal solution of succinyl chloride and glacial acetic acid, we get butyrolactone,  $C_2H_4\begin{smallmatrix} \diagup CH_2 \\ \diagdown CO \end{smallmatrix} O$  (p. 286), which was formerly considered succinic aldehyde,  $C_2H_4(CHO)_2$ .

Zinc ethide converts succinyl chloride into  $C_2H_4\begin{smallmatrix} \diagup C(C_2H_5)_2 \\ \diagdown CO \end{smallmatrix} O$ ,  $\gamma$ -diethyl-butyrolactone, which boils at  $230^\circ$ ; it forms salts of the corresponding acid with alkalies.

**Succinamide**,  $C_2H_4\begin{smallmatrix} \diagup CO.NH_2 \\ \diagdown CO.NH_2 \end{smallmatrix}$ , is produced by shaking succinic ester with aqueous ammonia. It is a white powder. It is insoluble in water and alcohol, and from hot water it crystallizes in needles. At  $200^\circ$  it decomposes into ammonia and succinimide.

**Succinimide**,  $C_2H_4\begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} NH$ . Gentle ignition of the anhydride in a current of dry ammonia or the distillation of ammonium succinate affords it. It crystallizes with 1 molecule of  $H_2O$  in rhombic plates, and dissolves readily in water and alcohol. It crystallizes from acetone in rhombic octahedra without any water. When anhydrous it melts at  $126^\circ$  and boils at  $288^\circ$ .

Succinimide combines with metallic oxides like those of silver and lead, exchanging its imide hydrogen for metals, for instance,  $C_2H_4\begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} NAg$ . The same compounds are obtained by the double decomposition of the potassium derivative with salts of the heavy metals (*Ann.*, 215, 200). The potassium compound,  $C_2H_4(CO)_2NK$  and  $C_2H_4(CO)_2K + \frac{1}{2}H_2O$ , is formed by adding alcoholic potash to an alcoholic solution of succinimide. Ether precipitates it, either as a powder or crystalline mass. The *silver salt*,  $C_2H_4(CO)_2NAg$  and  $C_2H_4(CO)_2NAg + \frac{1}{2}H_2O$ , crystallizes in silky needles.

*These compounds show that succinimide, like other imides, possesses an acidic character.*

It is not only the carboxyl group that determines the acid character of the carbon compounds; the imide group,  $NH$ , also seems capable of exchanging hydrogen for metals (forming salts), if it be attached to one or two carbonyl groups,  $CO$  (as in  $CO = NH$ ,

cyanic acid, and in  $\begin{smallmatrix} \text{CO} \\ \diagup \end{smallmatrix} \text{NH}$ ). This is particularly manifest in the urea derivatives of the dicarboxylic acids (see these).

**Methyl Succinimide**,  $\text{C}_2\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_3$ , is obtained by distilling methylamine succinate. It crystallizes in leaflets, melts at  $66.5^\circ$  and boils at  $234^\circ$ .

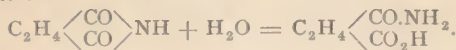
**Ethyl Succinimide**,  $\text{C}_2\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{N} \cdot \text{C}_2\text{H}_5$ , crystallizes in broad needles, which dissolve easily in water, alcohol and ether. It melts at  $26^\circ$  and boils at  $234^\circ$ .

On distilling succinimide with zinc dust, oxygen is withdrawn and pyrrol,  $\text{C}_4\text{H}_5\text{N}$  (see this) formed:—



Ethyl pyrrol,  $\text{C}_4\text{H}_4\text{N}(\text{C}_2\text{H}_5)$ , is obtained in a similar manner from ethyl succinimide.

**Succinamic Acid**,  $\text{C}_2\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH}_2 \\ \diagdown \text{CO} \cdot \text{OH} \end{smallmatrix}$ , is produced by heating succinimide with baryta water:—



It is crystalline, and water decomposes it with ease into succinic acid and ammonia.

**Mono- and Dibrom-succinic Acids** are formed when succinic acid, bromine and water are heated to  $150$ – $180^\circ$  in sealed tubes. The first is the chief product when an excess of water is used. The bromine is more readily introduced into succinic esters, or succinyl chloride, or the anhydride (p. 178). It is not even necessary to use the last two compounds as such; it will suffice to warm the succinic acid with amorphous phosphorus and water (*Ber.*, 14, 892).

**Monobrom-succinic Acid**,  $\text{C}_2\text{H}_3\text{Br} \begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$ , is obtained by the union of fumaric or maleic acid with  $\text{HBr}$  ( $\text{C}_4\text{H}_4\text{O}_4 + \text{HBr} = \text{C}_4\text{H}_5\text{BrO}_4$ ). It crystallizes in warty masses, consisting of minute needles, and is readily soluble in water. It melts at  $160^\circ$ , and decomposes into  $\text{HBr}$  and fumaric acid. It suffers similar decomposition when heated with water. On boiling with moist silver oxide it yields oxysuccinic acid,  $\text{C}_2\text{H}_3(\text{OH})(\text{CO}_2\text{H})_2$  (Malic Acid).

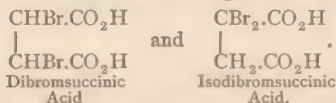
**Dibrom-succinic Acid**,  $\text{C}_2\text{H}_2\text{Br}_2(\text{CO}_2\text{H})_2$ , results by the direct union of fumaric acid with bromine. It may be obtained by heating succinic acid (12 parts) with bromine (33 parts) and water (12 parts) to  $150$ – $180^\circ$ , until all the bromine has disappeared, or by warming succinic acid with bromine in the presence of phosphorus (see above). It consists of prisms which are not very soluble in cold water. When heated to  $200$ – $235^\circ$  it breaks up into  $\text{HBr}$  and brom-maleic acid. Boiling water decomposes its salts; the silver salt yields dioxysuccinic acid (inactive tartaric acid), the sodium salt monobrom-malic acid,  $\text{C}_2\text{H}_2\text{Br}(\text{OH})(\text{CO}_2\text{H})_2$ , and the barium salt, inactive tartaric acid and monobrom-maleic acid,  $\text{C}_2\text{HBr}(\text{CO}_2\text{H})_2$ . When dibromsuccinic acid is heated with a solution of potassium iodide it becomes fumaric acid; boiling water decomposes it into  $\text{HBr}$  and brom-maleic acid. The methyl ester,  $\text{C}_2\text{H}_4\text{Br}_2(\text{CO}_2\text{CH}_3)_2$ , melts at  $62^\circ$ ; the ethyl ester at  $68^\circ$ , and when distilled it suffers decomposition (*Ber.*, 15, 1844).

**Isodibrom-succinic Acid**,  $C_2H_2Br_2(CO_2H)_2$ , is isomeric with the preceding. It is obtained in slight quantity by adding bromine to succinic acid, but is better prepared by the addition of  $Br_2$  to maleïc acid (see this). It is crystalline and very soluble in water. It melts at  $160^\circ$  and decomposes at  $180^\circ$ , or by boiling with water, into  $HBr$  and so-called isobrom-maleïc acid (p. 336). Silver oxide and water convert it into inactive tartaric acid. Sodium amalgam changes it to succinic acid. When warmed with a solution of potassium iodide it passes into fumaric acid.

The *esters* of this acid are prepared by conducting  $HCl$  into the alcoholic solution of the acid. They are liquids, and decompose when heated. The anhydride,  $C_2H_2Br_2(CO)_2O$ , results on heating maleïc anhydride,  $C_2H_2(CO)_2O$ , to  $100^\circ$  with bromine (dissolved in chloroform). It crystallizes in tables, melts at  $42^\circ$ , and at  $100^\circ$  decomposes into  $HBr$  and brom-maleïc anhydride. It readily unites with water to yield isodibrom-succinic acid.

Both dibrom-acids are converted by alcoholic potash into acetylene dicarboxylic acid,  $C_2(CO_2H)_2$  (p. 339).

It is generally assumed that the two dibrom-acids are derived from ordinary succinic acid and correspond to the formulas:—



It appears probable, however, that the one acid springs from ordinary succinic acid, and the other from the iso-acid, or that the same relations exist between them that we find existing between maleïc and fumaric acids (p. 334).

**Tribrom-succinic Acid**,  $C_2HBr_3(CO_2H)_2$ , is produced when bromine (and water) acts upon brom-maleïc acid and isobrom-maleïc acid; it consists of acicular crystals, which melt at  $136-137^\circ$ . The aqueous solution decomposes at  $60^\circ$  into  $CO_2$ ,  $HBr$ , and dibromacrylic acid,  $C_3H_2Br_2O_2$ , which melts at  $85^\circ$ .

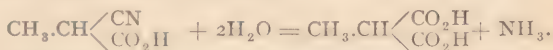
**Sulphono-succinic Acid**,  $C_2H_3\left\{\begin{array}{c} (CO_2H) \\ SO_3H \end{array}\right\}_2$ , is obtained by dissolving succinic acid in fuming sulphuric acid, or by the union of fumaric or maleïc acid with primary alkali sulphites. It is tribasic.

**Di-isonitroso-succinic Acid**,  $\begin{array}{c} C(N.OH).CO_2H \\ C(N.OH).CO_2H \end{array}$ , is formed by acting upon tetraoxysuccinic acid with hydroxylamine. It crystallizes in prisms and melts with decomposition at  $128-130^\circ$  (*Ber.* 16, 2985).

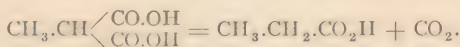
**Amido-succinic acid** (aspartic acid),  $C_2H_3(NH_2)(CO_2H)_2$ , and **amido-succinamic acid** (asparagine),  $C_2H_3(NH_2)\left\langle \begin{array}{c} CO_2H \\ CO_2.NH_2 \end{array} \right\rangle$ , will be described under malic acid, as they bear the same relation to it that glycocoll (amido-acetic) does to glycollic acid.

**Diamido-succinic Acid**,  $C_2H_2(NH_2)_2\left\langle \begin{array}{c} CO_2H \\ CO_2H \end{array} \right\rangle$ . Its diethyl ester is formed on treating dibrom-succinic ester with alcoholic ammonia. It crystallizes in needles or prisms, melts at  $122^\circ$ , and when saponified with alcoholic alkalies, yields the *free* diamido-acid. The latter is soluble in water, alcohol and ether and melts at  $151^\circ$  (*Ber.* 15, 1848, 14, 1713). Diamido-succinic acid is a diglycocoll (p. 290).

(2) **Isosuccinic Acid**,  $\text{CH}_3\cdot\text{CH}\begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$ , ethidene dicarboxylic acid, is obtained from  $\alpha$ -chlor- and brompropionic acids through the cyanide (*Ber.* 13, 209):—



When ethidene bromide,  $\text{CH}_3\cdot\text{CHBr}_2$  is heated with potassium cyanide and alkalis, we do not obtain ethidene succinic acid by the operation, but ordinary ethylene succinic acid. When malonic esters are treated with sodium and methyl iodide they yield isosuccinic acid. The latter crystallizes in needles or prisms, and is more readily soluble than ordinary succinic acid (in 4 parts  $\text{H}_2\text{O}$ ). It sublimes below  $100^\circ$  in plates, melts at  $130^\circ$ , and by further application of heat breaks up into  $\text{CO}_2$  and propionic acid (p. 316):—

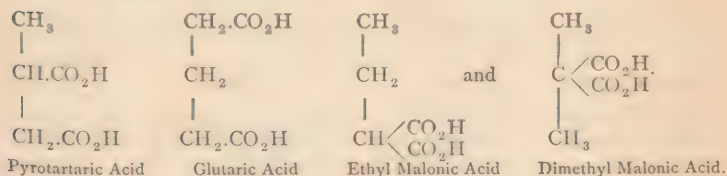


When heated with water above  $100^\circ$  the result is the same. The *ethyl ester*,  $\text{C}_4\text{H}_4\text{O}_4(\text{C}_2\text{H}_5)_2$ , boils at  $196^\circ$ .

*Brom-isosuccinic Acid*,  $\text{CH}_3\cdot\text{CBr}(\text{CO}_2\text{H})_2$ , is formed on heating isosuccinic acid with water and bromine to  $100^\circ$ . Large deliquescent prisms, which decompose readily.

(4) **Pyrotartaric Acids**,  $\text{C}_5\text{H}_8\text{O}_4 = \text{C}_3\text{H}_6\begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$ .

Four of these acids are theoretically possible:



(1) **Pyrotartaric Acid**,  $\text{CH}_3\cdot\text{CH}\begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CH}_2\cdot\text{CO}_2\text{H} \end{smallmatrix}$ , propylene dicarboxylic acid, was first obtained in the dry distillation of tartaric acid (mixed with pumice stone). It may be synthetically prepared from propylene bromide, by means of the cyanide:—



or by the action of nascent hydrogen upon the three isomeric acids: ita-, citra-, and mesa-conic acids:  $\text{C}_5\text{H}_6\text{O}_4 + \text{H}_2 = \text{C}_5\text{H}_8\text{O}_4$ . It is further formed from  $\alpha$ - and  $\beta$ -methyl aceto-succinic esters (made by introducing methyl into aceto-succinic esters and



by acting on aceto-acetic esters with  $\alpha$ -bromopropionic esters, p. 222); from  $\beta$ -brombutyric acid by means of the cyanide, and by heating pyroracemic acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , alone to  $170^\circ$ , or with hydrochloric acid to  $100^\circ$ . The acid consists of small, rhombic prisms, which dissolve readily in water, alcohol and ether. It melts at  $112^\circ$  and when quickly heated above  $200^\circ$  decomposes into water and the anhydride. If, however, it be exposed for some time to a temperature of  $200$ – $210^\circ$  it splits into  $\text{CO}_2$  and butyric acid. It suffers the same decomposition when in aqueous solution, if acted upon by sunlight in presence of uranium salts.

The neutral *calcium salt*,  $\text{C}_5\text{H}_6\text{O}_4\text{Ca} + 2\text{H}_2\text{O}$ , is difficultly soluble in water. The same may be remarked of the *acid potassium salt*,  $\text{C}_5\text{H}_7\text{KO}_4$ . The *ethyl ester* boils at  $218^\circ$ .

The *anhydride*,  $\text{CH}_3\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CO} \\ \text{CH}_2\cdot\text{CO}\end{smallmatrix}\right\rangle\text{O}$ , is a heavy oil, which boils at  $244.9^\circ$ , sinks in water and gradually reverts to the acid (*Ann.*, 191, 48).

(2) **Glutaric Acid**,  $\text{CH}_2\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CO}_2\text{H} \\ \text{CH}_2\cdot\text{CO}_2\text{H}\end{smallmatrix}\right\rangle$ , was first obtained by the reduction of  $\alpha$ -oxyglutaric acid with hydriodic acid. It may be synthetically prepared from trimethylene bromide (p. 74) through the cyanide; from aceto-acetic ester by means of the aceto-glutaric ester (p. 223), and from glutaconic acid (p. 337). Glutaric acid crystallizes in large monoclinic plates, melts at  $97^\circ$ , and distils near  $303^\circ$ , with scarcely any decomposition. It is soluble in 1.2 parts water of  $14^\circ$ .

The *calcium salt*,  $\text{C}_5\text{H}_6\text{O}_4\text{Ca} + 4\text{H}_2\text{O}$ , and *barium salt*,  $\text{C}_5\text{H}_6\text{O}_4\text{Ba} + 5\text{H}_2\text{O}$ , are easily soluble in water; the first more readily in cold than in warm water. The *ethyl ester*,  $\text{C}_5\text{H}_6\text{O}_4(\text{C}_2\text{H}_5)_2$ , boils at  $237^\circ$ . The *anhydride*,  $\text{C}_5\text{H}_6\text{O}_3$ , forms on slowly heating the acid to  $230$ – $280^\circ$ , and in the action of acetyl chloride on the silver salt of the acid. It crystallizes in needles, melting at  $56$ – $57^\circ$  (after solidification it melts at  $36^\circ$ ), and boils near  $285^\circ$ .

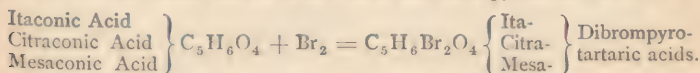
*Glutarimide*,  $\text{C}_3\text{H}_6(\text{CO})_2\text{NH}$ , results by the distillation of ammonium glutarate. It crystallizes in shining leaflets and melts at  $152^\circ$ . The vegetable alkaloid piperidine,  $\text{C}_5\text{H}_{10}\text{NH}$ , is obtained from it by distilling with zinc dust.  $\text{PCl}_5$  and  $\text{HI}$  convert it into the base *pyridine*,  $\text{C}_5\text{H}_7\text{N}$ , just as succinimide yields pyrrol (p. 327) (*Ber.*, 16, 1683).

(3) **Ethyl Malonic Acid**,  $\text{C}_2\text{H}_5\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CO}_2\text{H} \\ \text{CO}_2\text{H}\end{smallmatrix}\right\rangle$ , is obtained from  $\alpha$ -brombutyric ester, through the cyanide, and by the action of  $\text{Na}$  and  $\text{C}_2\text{H}_5\text{I}$  upon malonic ester. It is very similar to ordinary tartaric acid, melts at  $111.5^\circ$  and decomposes at  $160^\circ$ , more rapidly at  $170^\circ$ , into butyric acid and  $\text{CO}_2$ . The *calcium salt*,  $\text{C}_5\text{H}_6\text{O}_4\text{Ca} + \text{H}_2\text{O}$ , forms prisms, and is more easily soluble in cold than in hot water. Its *ethyl ester* boils at  $200^\circ$ .

(4) **Dimethyl Malonic Acid**,  $\text{CH}_3\left\langle\begin{smallmatrix}\text{CH}_3 \\ \text{CH}_3\end{smallmatrix}\right\rangle\text{C}\left\langle\begin{smallmatrix}\text{CO}_2\text{H} \\ \text{CO}_2\text{H}\end{smallmatrix}\right\rangle$ , is obtained from  $\alpha$ -bromisobutyric ester by means of potassium cyanide; by introducing methyl into malonic ester, and from mesitylenic acid (*Ber.*, 15, 581). It crystallizes in four-sided

prisms, and is difficultly soluble in alcohol, but rather readily soluble in water. It is not as soluble as its isomerides. It sublimes about  $120^{\circ}$  and melts at  $170^{\circ}$ , decomposing at the same time into  $\text{CO}_2$  and isobutyric acid. The *barium salt* crystallizes in needles; the *calcium salt* is more soluble in cold than in warm water. The *ethyl ester* boils at  $195^{\circ}$ .

The isomeric chlorine and bromine substitution products of the pyrotartaric acids are produced by the direct addition of  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{Br}_2$ , to the unsaturated isomeric acids,  $\text{C}_5\text{H}_6\text{O}_4$ : itaconic, citraconic and mesaconic acids (p. 338). The new derivatives are known as ita-, citra- and mesa-pyrotartaric acids:—



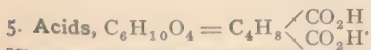
**Itachlor-pyrotartaric Acid** is formed by heating itaconic acid with fuming hydrochloric acid to  $130^{\circ}$ . It melts at  $145^{\circ}$ . When heated with water or alkalies it passes into itamalic acid,  $\text{C}_5\text{H}_7(\text{OH})\text{O}_4$ . It affords paraconic acid,  $\text{C}_5\text{H}_6\text{O}_4$ , with silver oxide.

**Citra- or Mesa-chlorpyrotartaric Acid** is obtained on treating citraconic anhydride with cold concentrated hydrochloric acid, and by heating mesaconic acid to  $140^{\circ}$  with concentrated hydrochloric acid. It crystallizes in plates and melts at  $129^{\circ}$ . When boiled with water it breaks up into  $\text{HCl}$  and mesaconic acid. Boiling alkalies change it into  $\text{HCl}$ ,  $\text{CO}_2$  and methacrylic acid,  $\text{C}_4\text{H}_6\text{O}_2$ .

Fuming hydrobromic acid converts citraconic acid, its anhydride and also mesaconic acid (at  $140^{\circ}$ ) into the same **brompyrotartaric acid**,  $\text{C}_5\text{H}_7\text{BrO}_4$ . It melts at  $148^{\circ}$ , and when boiled with water yields  $\text{CO}_2$ ,  $\text{HBr}$  and methacrylic acid. **Itabrompyrotartaric acid**, from itaconic acid, is not so soluble in water, and melts at  $137^{\circ}$ .

The ita-, citra- and mesa-dibrompyrotartaric acids,  $\text{C}_5\text{H}_6\text{Br}_2\text{O}_4$ , are distinguished by their different solubility in water. The ita- compound changes to aconic acid,  $\text{C}_5\text{H}_4\text{O}_4$ , when the solution of its sodium salt is boiled; the citra- and mesa- compounds, on the other hand, yield brom-methacrylic acid (p. 193).

Nascent hydrogen causes all these substitution derivatives to revert to ordinary pyrotartaric acid.

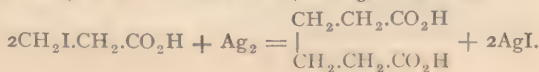


Nine are possible and eight known: (1) Normal Butandicarboxylic acid or Adipic acid. (2)  $\alpha$ - and  $\beta$ -Methyl glutaric acids (isomerides), derived from glutaric acid,  $\text{CH}_2 \begin{array}{l} \swarrow \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \searrow \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$ . (3)  $\alpha$ - and  $\beta$ -Dimethyl succinic acids and

ethyl succinic acid (isomerides) derived from succinic acid,  $\begin{array}{l} \text{CH}_2 \cdot \text{CO}_2\text{H} \\ | \\ \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$ .

(4) Propyl, isopropyl, and methyl-ethyl malonic acids (isomerides), derived from malonic acid.

(1) **Adipic Acid**,  $\text{C}_6\text{H}_{10}\text{O}_4$ , was first obtained by oxidizing fats with nitric acid. It is synthetically prepared by heating  $\beta$ -iodopropionic acid, with reduced silver, to  $130$ – $140^{\circ}$ :—



It is also obtained by the action of nascent hydrogen upon hydro-muconic acid,  $C_6H_8O_4$  (p. 338), and by oxidizing sebacylic acid with nitric acid (along with succinic acid). It crystallizes in shining leaflets or prisms, which dissolve in 13 parts cold water, and melt at  $148^\circ$ .

(2)  **$\alpha$ -Methyl Glutaric Acid**,  $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot CO_2H \\ \diagdown CH(CH_3) \cdot CO_2H \end{smallmatrix}$ , is obtained from methyl aceto-acetic ester, by the action of  $\beta$ -iodopropionic ester and the elimination of ketone (p. 315), and by the reduction of saccharon. It melts at  $76^\circ$ . The  $\beta$ -acid,  $CH_3 \cdot CH \begin{smallmatrix} \diagup CH_2 \cdot CO_2H \\ \diagdown CH_2 \cdot CO_2H \end{smallmatrix}$ , from ethidene dimalonic acid (*Ann.*, 218, 161), melts at  $86^\circ$ , and forms an anhydride, which melts at  $46^\circ$  and boils at  $283^\circ$ .

(3) **Symm. Dimethyl Succinic Acid**,  $\begin{smallmatrix} CH_3 \cdot CH \cdot CO_2H \\ | \\ CH_3 \cdot CH \cdot CO_2H \end{smallmatrix}$ , is derived from  $\alpha$ -bromopropionic acid,  $CH_3 \cdot CHBr \cdot CO_2H$ , by the action of reduced silver (analogous to  $\alpha$ -adipic acid); and from aceto-acetic ester, by means of  $\alpha$ -bromopropionic ester and methyl iodide (p. 223). It melts at  $165$ – $167^\circ$ .

**Unsymm.  $\beta$ -Dimethyl Succinic Acid**,  $\begin{smallmatrix} CH_2 \cdot CO_2H \\ | \\ (CH_3)_2 - C \cdot CO_2H \end{smallmatrix}$ , is obtained by the action of hydriodic acid or sodium amalgam upon pyrocinehonic acid (dimethyl fumaric acid, p. 338); also from cyanethine (p. 243). It crystallizes in prisms, melts at  $192^\circ$ , and sublimates at  $100^\circ$  (*Ber.*, 16, 83).

**Ethyl Succinic Acid**,  $C_2H_3(C_2H_5)(CO_2H)_2$ , melts at  $98^\circ$ .

(4) **Isopropyl Malonic Acid**,  $C_3H_7 \cdot CH \begin{smallmatrix} \diagup CO_2H \\ \diagdown CO_2H \end{smallmatrix}$ , from sodium malonic ester, melts at  $87^\circ$ , and at  $150^\circ$  breaks up into  $CO_2$  and normal valeric acid. **Methyl-ethyl Malonic Ester**,  $\begin{smallmatrix} CH_3 \\ \diagdown \\ C_2H_5 \end{smallmatrix} \begin{smallmatrix} \diagup C(CO_2H)_2 \end{smallmatrix}$ , melts at  $118^\circ$ , and decomposes into  $CO_2$ , and methyl-ethyl acetic acid.

## 6. Acids, $C_7H_{12}O_4 = C_5H_{10}(CO_2H)_2$ .

**Propyl Succinic Acid**,  $C_3H_7 \cdot CH \begin{smallmatrix} \diagup CH_2 \cdot CO_2H \\ \diagdown CO_2H \end{smallmatrix}$ , from propyl-ethylene tricarboxylic ester (*Ann.*, 214, 54), crystallizes in warty masses, and melts at  $91^\circ$ .

**Isopropyl Succinic Acid**,  $(CH_3)_2 \cdot CH \cdot CH \begin{smallmatrix} \diagup CH_2 \cdot CO_2H \\ \diagdown CO_2H \end{smallmatrix}$ , **Pimelic Acid**, was first prepared by fusing camphoric acid, and may be synthetically obtained from aceto-acetic or malonic esters (*Ber.*, 16, 2622; *Ann.*, 220, 271). It forms crusts, is readily soluble in water, alcohol, and ether, melts at  $114^\circ$ , and on stronger heating yields an anhydride. **Diethyl Malonic Acid**,  $(C_2H_5)_2 \cdot CH(CO_2H)_2$ , from ethyl malonate, melts at  $121^\circ$ , and at  $175^\circ$  decomposes into  $CO_2$  and diethyl acetic acid.

**Propidene Diacetic Acid**,  $C_2H_5 \cdot CH(CH_2 \cdot CO_2H)_2$ , from propidene dimalonic acid (*Ann.*, 218, 167), melts at  $67^\circ$ .

So-called  **$\alpha$ -Pimelic Acid**,  $C_5H_{10}(CO_2H)_2$ , results from the oxidation of suberone,  $C_7H_{12}O$ , and on heating furonic acid with hydriodic acid. It crystallizes in large plates, and melts at  $100^\circ$ .

Higher dibasic acids are produced by oxidizing the fatty acids or oleic acids with nitric acid. They always form succinic and oxalic acids at the same time. The acids of the series,  $C_nH_{2n-4}O_4$  (p. 197) usually decompose into the acids  $C_nH_{2n}O_4$ , when oxidized with fuming nitric acid. The mixture of acids that results is separated by fractional crystallization from ether; the higher members, being less soluble, separate out first (*Ber.*, 14, 560).

**Suberic Acid**,  $C_8H_{14}O_4$ , is obtained by boiling corks or fatty oils with nitric acid (*Ber.*, 13, 1165). It forms long needles or plates, melts at  $140^\circ$ , and sublimes undecomposed. It dissolves in 200 parts of cold water, more readily in hot water, alcohol and ether. Its *ethyl ester* boils at  $280-282^\circ$ . By distilling the

calcium salt we get  $C_6H_{14}$ , hexane, and  $C_7H_{12}O = \begin{matrix} CH_2 \cdot CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \cdot CH_2 \end{matrix} > CO$ ,

**Suberone** (*Ann.*, 211, 117), a liquid with an odor like that of peppermint, and boiling at  $180^\circ$ .

An isomeric acid, tetramethyl succinic acid,  $(CH_3)_2C.CO_2H$ , is obtained on heating bromisobutyric acid,  $(CH_3)_2C.Br.CO_2H$ , with reduced silver. It melts at  $95^\circ$ , and dissolves in 45 parts water at  $10^\circ$ . A third isomeride, diethyl

succinic acid,  $C_2H_5.CH.CO_2H$ , is obtained from  $\alpha$ -brombutyric acid,  $C_2H_5.CHBr.CO_2H$ , with silver; its ethyl ester boils at  $233-235^\circ$ .

**Lepargylic Acid**,  $C_9H_{16}O_4$ , **Azelaic Acid**, is best prepared by oxidizing castor oil (*Ber.*, 14, 560). It crystallizes in shining leaflets, resembling benzoic acid. It melts at  $106^\circ$ , and dissolves in 100 parts cold water.

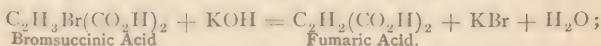
**Sebacic Acid**,  $C_{10}H_{18}O_4$ , is obtained by the dry distillation of oleic acid, by the oxidation of stearic acid and spermaceti, and by fusing castor oil with caustic potash. It crystallizes in shining laminae, which melt at  $127^\circ$ .

**Brassylic Acid**,  $C_{11}H_{20}O_4$ , obtained by oxidizing behenoleic and erucic acids, melts at  $108^\circ$ , and is almost insoluble in water.

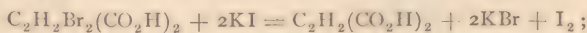
**Roccellic Acid**,  $C_{17}H_{32}O_4$ , occurs free in *Rocella tinctoria*. Prisms melting at  $132^\circ$ .

## UNSATURATED DICARBOXYLIC ACIDS, $C_nH_{2n-4}O_4$ .

The acids of this series bear the same relation to those of the oxalic acid series as the acids of the acrylic series do to the fatty acids. They can be obtained from the saturated dicarboxylic acids by the withdrawal of two hydrogen atoms. This is effected by acting on the monobrom-derivatives with alkalis:—



or, the same result is reached by letting potassium iodide act upon the dibrom-derivatives (p. 189). Thus, fumaric acid is formed from both dibrom- and isodibrom-succinic acids:—



and mesaconic acid,  $C_3H_4(CO_2H)_2$ , from citra- and mesa-dibrom-pyrotartaric acids,  $C_3H_4Br_2(CO_2H)_2$ . As a general thing the unsatu-



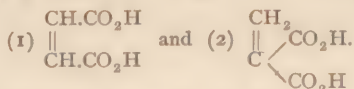
rated acids are obtained from the oxydicarboxylic acids by the elimination of water (p. 190).

The esters of these acids are obtained in the condensation of malonic esters with aldehydes:—



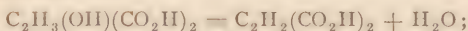
Ethidene malonic esters are formed at the same time; from them we can get saturated dicarboxylic acids (*Ann.*, 218, 156).

The isomerisms of the acids of this series offer peculiar relations, as yet unexplained. The lowest member of the series has the formula  $\text{C}_2\text{H}_2(\text{CO}_2\text{H})_2$ . This can be structurally represented in two ways:—

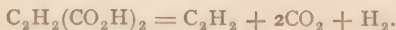


The first would correspond to succinic acid, the second to the iso-acid. Two acids—maleïc and fumaric—with the formula  $\text{C}_2\text{H}_2(\text{CO}_2\text{H})_2$ , are known. Owing to its ability to form an anhydride maleïc acid is supposed to have the first structural formula. (The supposition that a divalent carbon atom is present in the acid offers no explanation for its behavior.) The second formula is then ascribed to fumaric acid. Certain synthetic methods (p. 335) used in forming these acids argue for the preceding views. Yet the most of the transpositions suffered would seem to show that the acids have the same structural formula, that the acid  $\text{CH}_2\text{:C}(\text{CO}_2\text{H})$  is very unstable, and inclined to polymerize, and that relations exist between the two acids, similar to those noticed with the crotonic acids (p. 193) and some other isomeric compounds, and for which our present structural formulas offer no expression. The numerous and readily occurring transpositions of these acids into each other (see below) enhance the difficulty in giving an answer to these questions.

1. **Fumaric and Maleïc Acids**,  $\text{C}_2\text{H}_2\begin{array}{c} \nearrow \text{CO}_2\text{H} \\ \searrow \text{CO}_2\text{H} \end{array}$ , are obtained by distilling malic acid:—



fumaric acid remains in the residue, while maleïc acid and its anhydride pass over into the receiver (*Ber.*, 12, 2281). The two latter are formed in especially large quantities on rapidly heating malic acid, whereas, by prolonged heating at  $150^\circ$ , fumaric acid is the chief product. If maleïc acid be heated for some time at  $130^\circ$  it changes to fumaric acid; when the latter is distilled it decomposes into water and maleïc anhydride. Acetylene is obtained by the electrolysis of a concentrated solution of the sodium salts of the two acids (p. 61):—



We can obtain maleïc acid (its ester) synthetically by heating dichloroacetic ester,  $\text{CHCl}_2\text{.CO}_2\text{.C}_2\text{H}_5$ , with silver or sodium. Fumaric acid is formed from

$\alpha,\beta$ -dichloropropionic acid (which yields  $\alpha$ -chloracrylic acid,  $\text{CH}_2\text{:CCl.CO}_2\text{H}$ , p. 191), by the action of potassium cyanide and caustic potash. Both syntheses indicate that the first formula properly falls to maleïc acid and the second to fumaric (p. 334). This conclusion is contradicted by the formation of maleïc acid from  $\beta$ -dibromopropionic acid (which yields  $\alpha$ -bromacrylic acid,  $\text{CH}_2\text{:CBr.CO}_2\text{H}$ , p. 191), by the action of potassium cyanide and potash, and fumaric acid from chlorethenyl tricarboxylic ester,  $\text{C}_2\text{H}_2\text{Cl}(\text{CO}_2\text{.C}_2\text{H}_5)_3$ , (*Ber.*, 13, 100 and 2163); also, by the fact that fumaric acid is formed from dichloroacetic and malonic acids (*Ann.*, 218, 169).

**Fumaric Acid** occurs free in many plants, in Iceland moss, in *Fumaria officinalis* and in some fungi. It is produced by heating dibrom- and isodibrom-succinic acids with a solution of potassium iodide; and from monobrom- and sulpho-succinic acids by fusion with potash. It is almost insoluble in water. Mineral acids precipitate it from solutions of its alkali salts as a white crystalline powder. It crystallizes from hot water in small, striated prisms. It has a very acid taste, and dissolves readily in alcohol and ether. It melts with difficulty, sublimes at  $200^\circ$ , forming maleïc anhydride and water. Sodium amalgam, hydriodic acid and other reducing agents convert it into succinic acid. Metallic zinc combines with fumaric acid in the presence of water, forming zinc succinate:  $\text{C}_4\text{H}_4\text{O}_4 + \text{Zn} = \text{C}_4\text{H}_4\text{O}_4\text{Zn}$ .

Fuming  $\text{HBr}$  at  $100^\circ$  converts fumaric into monobromsuccinic acid. At ordinary temperatures it combines with bromine (and water) very slowly, more rapidly on heating to  $100^\circ$ , yielding dibromsuccinic acid. When fumaric acid is heated with caustic soda to  $100^\circ$ , or with water to  $150\text{--}200^\circ$ , it passes into inactive malic acid, which, at  $135^\circ$ , decomposes into water and maleïc acid. On oxidizing the acid with  $\text{MnO}_4\text{K}$  it affords racemic, whereas, maleïc acid forms inactive tartaric acid (*Ber.*, 14, 713).

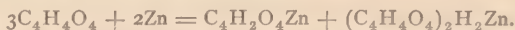
With the exception of the alkali, all the salts of fumaric acid are very difficultly soluble in water. The *silver salt*,  $\text{C}_4\text{H}_2\text{O}_4\text{Ag}_2$ , is perfectly insoluble; hence, silver nitrate will completely precipitate fumaric acid from even dilute solutions.

The *esters* are obtained from the silver salt by the action of alkyl iodides, and by leading  $\text{HCl}$  into the alcoholic solutions of fumaric and maleïc acids (*Ber.*, 12, 2283). They unite just as readily with  $2\text{Br}$  (forming esters of dibromsuccinic acid) as the esters of maleïc acid do.

The *methyl ester*,  $\text{C}_2\text{H}_2(\text{CO}_2\text{.CH}_3)_2$ , forms white needles, melting at  $102^\circ$ , and boiling at  $192^\circ$ . The *ethyl ester* is liquid, and boils at  $218^\circ$ . It can be obtained by the action of  $\text{PCl}_3$  upon esters of malic acid.

**Maleïc Acid** crystallizes in large prisms or plates, is very easily soluble in cold water, and possesses a peculiar taste. It melts at  $130^\circ$  and distils at  $160^\circ$ , decomposing partially into the anhydride and water. Heated for some time at  $130^\circ$ , or boiled with dilute sulphuric acid, or nitric acid, with  $\text{HBr}$  and  $\text{HI}$ , it changes to fumaric acid. Nascent hydrogen converts it into ordinary succinic acid. Metallic zinc dissolves in aqueous maleïc acid

without evolving hydrogen, and forms zinc maleate and acid zinc succinate:—



Fuming hydrobromic acid combines with maleïc acid at  $0^\circ$  and yields monobromsuccinic acid; an equivalent of fumaric acid forms at the same time. Bromine (and water) at ordinary temperature converts the acid into isodibrom-succinic and fumaric acids.

The *esters* are produced in the same manner as those of the preceding acid. Traces of iodine will change them, on warming, into esters of fumaric acid. Bromine converts them into esters of dibrom-succinic acid; fumaric acid very probably appears at first.

The *methyl ester*,  $\text{C}_2\text{H}_2(\text{CO}_2\cdot\text{CH}_3)_2$ , is a liquid, and boils at  $205^\circ$ . The *ethyl ester* boils at  $225^\circ$ .

**Maleïc Anhydride—Maleyl Oxide**,  $\text{C}_4\text{H}_2\text{O}_3 = \text{C}_2\text{H}_2\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{O}$ .

This is produced by distilling maleïc or fumaric acid, or more readily by heating maleïc acid with acetyl chloride (p. 316); it is purified by crystallization from chloroform (*Ber.*, **12**, 2281, and **14**, 2546). It affords needles or prisms, which melt at  $53^\circ$  ( $60^\circ$ ) and boil at  $202^\circ$  ( $196^\circ$ ). It regenerates maleïc acid by union with water, and forms isodibromsuccinic anhydride when heated with bromine to  $100^\circ$ .

**Brom-maleïc Acid**,  $\text{C}_4\text{H}_3\text{BrO}_4$ , is produced by boiling barium dibromsuccinate or the free acid with water. It affords prisms melting at  $128^\circ$ . **Brom-fumaric Acid**,  $\text{C}_4\text{H}_3\text{BrO}_4$ , called isobrommaleïc acid, is formed, the same as the preceding, from isodibromsuccinic acid or its barium salt, or by the addition of  $\text{HBr}$  to acetylene dicarboxylic acid (p. 339). It consists of very soluble leaflets, which melt at  $177$ – $178^\circ$ .

These two brom-acids conduct themselves toward bromine and  $\text{HBr}$  the same as maleïc and fumaric acids. When boiled with  $\text{HBr}$  brommaleïc acid is converted into bromfumaric acid; its esters, too, change to those of bromfumaric acid when they are heated with iodine. Sodium amalgam changes both to fumaric and subsequently to succinic acid. By distillation, both yield water and brom-maleïc anhydride,  $\text{C}_4\text{HBrO}_3$ . The latter readily unites with water, forming brom-maleïc acid (*Ann.*, **195**, 56).

**Dibrom-maleïc Acid**,  $\text{C}_2\text{Br}_2(\text{CO}_2\text{H})_2$ , is obtained by acting on succinic acid with  $\text{Br}$ , or by the oxidation of mucobromic acid with bromine water, silver oxide or nitric acid. It is very readily soluble, melts at  $120^\circ$ – $125^\circ$ , and readily forms the *anhydride*,  $\text{C}_2\text{Br}_2(\text{CO})_2\text{O}$ , which melts at  $115^\circ$ , and sublimes in needles (*Ber.*, **13**, 736). Its half-aldehyde is the so-called **mucobromic acid**,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_3 = \text{C}_2\text{Br}_2\langle\begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CHO} \end{smallmatrix}\rangle$ , which results from the action of bromine water upon pyromucic acid. It crystallizes in glistening laminae, and melts at  $120^\circ$ . When oxidized it is converted into dibrom-maleïc acid; baryta changes it to malonic, dibrom-acrylic and brompropionic acids.

The *dialdehyde* of dibrom-maleïc acid,  $\text{C}_2\text{Br}_2\langle\begin{smallmatrix} \text{CHO} \\ \text{CHO} \end{smallmatrix}\rangle$ , is produced when bromine water acts upon dibrompyromucic acid,  $\text{C}_3\text{H}_2\text{Br}_2\text{O}_3$ . It melts at  $88^\circ$ , and when oxidized yields mucobromic acid.

**Dichlormaleïc Acid**,  $C_2Cl_2(CO_2H)_2$ . Its *imide*,  $C_2Cl_2\begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} NII$ , is obtained when the perchlorpyrocoll and succinimide (p. 326) are heated in a current of chlorine. It consists of needles melting at  $179^\circ$ . Boiling caustic potash converts the imide into dichlormaleïc acid. This consists of deliquescent needles, which on the application of heat pass into the *anhydride*,  $C_2Cl_2(CO)_2O$ , which melts at  $120^\circ$ . When the imide is heated with water  $CO_2$  splits off and  $\alpha$ -dichloracrylic acid is produced (*Ber.*, 16, 2394; 17, 553).

The half aldehyde of dichlormaleïc acid is the so-called **mucochloric acid**,  $C_2Cl_2\begin{smallmatrix} \diagup CHO \\ \diagdown CO_2H \end{smallmatrix}$ . This is obtained when chlorine water acts upon pyromucic acid. It melts at  $125^\circ$ . Alkalies convert it into formic and  $\alpha$ -dichloracrylic acid.

## 2. Acids, $C_5H_6O_4 = C_3H_4(CO_2H)_2$ .

Five unsaturated dicarboxylic acids of this formula are known: ethidene malonic, glutaconic, itaconic, citraconic, mesaconic and crotaconic acid; the structure of all but the first is yet in doubt. The so-called vinylmalonic acid, obtained from ethylene bromide and the ester of malonic acid, is identical with  $\alpha$ -trimethylene dicarboxylic acid, derived from trimethylene.

**Ethidene Malonic Acid**,  $CH_3.CH:C(CO_2H)_2$ , is only known in its ethyl ester. This is formed by the condensation of malonic ester with acetaldehyde on heating with acetic anhydride (p. 334). It boils at  $220^\circ$ , and at  $118-120^\circ$  under a pressure of 21 mm. When saponified with baryta water it yields an oxydicarboxylic acid, glutanic acid— $C_3H_5(OH)(CO_2H)_2$ . It combines with malonic ester on heating, and becomes ethidene dimalonic ester (*Ann.*, 218, 161).

**Glutaconic Acid**,  $CH\begin{smallmatrix} \diagup CH_2.CO_2H \\ \diagdown CH.CO_2H \end{smallmatrix}$ , arises in the saponification of the dicarboxy-glutaconic ester (obtained from the ester of malonic acid and chloroform, *Ann.*, 222, 249). It melts at  $132^\circ$ . Sodium amalgam converts it into glutaric acid.

Citraconic and itaconic acids, judging from their behavior, bear the same relations to mesaconic acid, that maleïc sustains to fumaric acid. They afford anhydrides, whereas mesaconic acid when distilled passes into citraconic anhydride.

Citraconic and itaconic acid are obtained in the distillation of citric acid. Aconitic acid,  $C_6H_8(CO_2H)_3$  (see this), is produced at first and by the subsequent withdrawal of water and  $CO_2$  it yields itaconic and citraconic anhydrides:  $C_6H_8O_6 = C_5H_4O_3 + H_2O + CO_2$ . Both anhydrides are present in the filtrate. The first yields itaconic acid by union with water (*Ber.*, 13, 1541). When free itaconic acid is distilled it affords water and citraconic anhydride, which changes to the acid on warming with water. If citraconic acid be heated for some time to  $100^\circ$  or its aqueous solution to  $130^\circ$ , itaconic acid is produced. Boiling dilute nitric acid or concentrated haloid acids convert citraconic into mesaconic acid.

Citra-, ita-, and mesaconic acids unite with chlorine, bromine and the halogen hydrides, yielding derivatives of pyrotartaric acid (p. 329); the first two acids react in the cold; mesaconic acid (like fumaric acid) only on the application of heat. Nascent hydrogen converts them all into the same pyrotartaric acid. The electrolysis of their sodium salts (p. 61) decomposes them, according to the equation:—





when ordinary allylene,  $\text{CH}_3\text{C}:\text{CH}$ , results from citra- and itaconic acid, and isoallylene (p. 63) from itaconic acid.

**Citraconic Acid**,  $\text{C}_5\text{H}_6\text{O}_4$ , is obtained from its anhydride by heating the latter with water. It crystallizes in glistening prisms, which deliquesce in the air, and melt at  $80^\circ$ . It breaks up on distillation into its anhydride and water. **Citraconic Anhydride**,  $\text{C}_5\text{H}_4\text{O}_3$ , is also formed by heating the acid with acetyl chloride, and is obtained by the repeated distillation of the distillate (see above) resulting from citric acid. It is an oily liquid which boils at  $213\text{--}214^\circ$  with partial transformation into xeronic anhydride (see below); it combines to citraconic acid when heated with water.

**Itaconic Acid**,  $\text{C}_5\text{H}_6\text{O}_4$ , is best obtained by heating citraconic anhydride with 3–4 parts water to  $150^\circ$ . It crystallizes in rhombic octahedra, dissolves in 17 parts  $\text{H}_2\text{O}$  at  $10^\circ$ , melts at  $161^\circ$  and decomposes when distilled into citraconic anhydride and water. **Itaconic Anhydride**,  $\text{C}_5\text{H}_4\text{O}_3$ , is prepared from the acid on heating with acetyl chloride (*Ber.*, 13, 1541). It crystallizes from chloroform in rhombic prisms, melts at  $68^\circ$  and distils unaltered under diminished pressure, but at ordinary pressures changes to citraconic anhydride. It dissolves in water with formation of itaconic acid.

**Mesaconic Acid**,  $\text{C}_5\text{H}_6\text{O}_4$ , is prepared by heating citra- and itaconic acid with a little water to  $200^\circ$  and may be obtained by evaporating citraconic anhydride with dilute nitric acid (*Ann.*, 188, 73). It is rather difficultly soluble in water (47 parts at  $18^\circ$ ), crystallizes in glistening needles or prisms, melts at  $202^\circ$  and at  $205^\circ$  decomposes into citraconic anhydride and water.

Consult *Ber.* 14, 2785, for the esters of citra-, ita-, and mesaconic acids.

**Crotaconic Acid**,  $\text{C}_5\text{H}_6\text{O}_4$ , has been obtained from  $\beta$ -chlorcrotonic acid (p. 193) by means of potassium cyanide. It melts at  $119^\circ$  and at  $130^\circ$  breaks up into  $\text{CO}_2$  and crotonic acid.

(3) Acids,  $\text{C}_6\text{H}_8\text{O}_4 = \text{C}_4\text{H}_6(\text{CO}_2\text{H})_2$ .\*

**Allyl Malonic Acid**,  $\text{CH}_2:\text{CH}.\text{CH}_2.\text{CH}(\text{CO}_2\text{H})_2$ , is obtained from malonic ester by means of allyl iodide. It crystallizes in prisms and melts at  $103^\circ$  (*Annalen*, 216, 52). Hydrobromic acid converts it into carbovalerolactonic acid,  $\text{C}_6\text{H}_6\text{O}_3$  (the lactone of  $\gamma$ -oxypropio-malonic acid) (p. 275):—



The latter is a thick liquid, readily soluble in water. When heated to  $200^\circ$  it breaks up into  $\text{CO}_2$  and valerolactone (p. 287).

**Hydromuconic Acid**,  $\begin{array}{c} \text{CH}.\text{CH}_2.\text{CO}_2\text{H} \\ || \\ \text{CH}.\text{CH}_2.\text{CO}_2\text{H} \end{array}$ , is formed by the action of sodium amalgam upon chlormuconic acid,  $\text{C}_6\text{H}_4\text{Cl}_2\text{O}_4$ . The latter is obtained from mucic acid by the action of  $\text{PCl}_5$ . The chloride,  $\text{C}_6\text{H}_2\text{Cl}_2\text{O}_2\text{Cl}_2$ , which first appears is decomposed with water. It consists of large prisms, difficultly soluble in water, and melting at  $195^\circ$ . Sodium amalgam converts it into adipic acid and bromine into dibromadipic acid.

**Dimethyl Fumaric Acid** (?),  $\begin{array}{c} \text{CH}_3.\text{C}.\text{CO}_2\text{H} \\ || \\ \text{CH}_3.\text{C}.\text{CO}_2\text{H} \end{array}$ , pyrocinchonic acid, is only

known in its salts and ethers. When separated from the latter it is at once transformed into the anhydride,  $\text{C}_6\text{H}_6\text{O}_3$ . The latter is obtained by oxidizing turpentine oil (together with terebic acid), by heating cinchonic acid,  $\text{C}_7\text{H}_6\text{O}_5$ , (with separa-

\* Tetramethylene dicarboxylic acid is isomeric with these unsaturated acids.

tion of  $\text{CO}_2$ ), and by heating  $\alpha$ -dichloropropionic acid,  $\text{CH}_3\text{CHCl}_2\text{CO}_2\text{H}$ , with reduced silver (*Berichte*, 15, 1320, 2347). The anhydride crystallizes from water in large pearly laminae, which melt at  $96^\circ$  and distil at  $223^\circ$ . The aqueous solution has a very acid reaction and decomposes alkaline carbonates. The salts have the formula,  $\text{C}_6\text{H}_6\text{O}_4\text{Me}_2$ ; its solutions acquire a dark-red color on the addition of ferric chloride. It is oxidized by a chromic acid mixture, and affords 2 molecules of acetic acid and 2 molecules of carbon dioxide. By the action of sodium amalgam, or by heating with hydriodic acid it is converted into unsymmetrical dimethylsuccinic acid (p. 332). An atomic rearrangement takes place here (*Berichte*, 15, 2013).

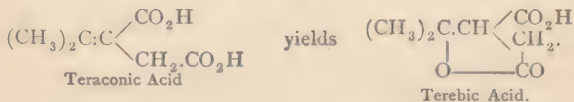
(4) **Acids**,  $\text{C}_7\text{H}_{10}\text{O}_4 = \text{C}_5\text{H}_8(\text{CO}_2\text{H})_2$ .

**Allyl Succinic Acid**,  $\text{C}_3\text{H}_5\text{CH} \begin{smallmatrix} \text{CH}_2\text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$ , results by the withdrawal of  $\text{CO}_2$  from allyl ethenyl tricarboxylic acid,  $\text{C}_3\text{H}_5\text{C}_2\text{H}_2(\text{CO}_2\text{H})_3$  (*Ber.* 16, 335). It crystallizes from alcohol in leaflets, melts at  $94^\circ$  and when heated above  $140^\circ$  passes into the corresponding anhydride,  $\text{C}_7\text{H}_8\text{O}_3$ —an oil boiling near  $250^\circ$ . Hydrobromic acid converts it into **Carbocaprolactonic Acid**,  $\text{C}_7\text{H}_{10}\text{O}_5$ , the lactone of  $\gamma$ -oxypropio-succinic acid:—



The latter melts at  $69^\circ$  and distils at  $260^\circ$  without decomposition.

**Teraconic Acid**,  $(\text{CH}_3)_2\text{C:C} \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CH}_2\text{CO}_2\text{H} \end{smallmatrix}$ , is produced in small quantity (together with pyroterebic acid (p. 195) in the distillation of terebic acid (*Ann.* 208, 50), and may be prepared by the action of sodium upon terebic esters (*Ann.* 220, 254). It melts at  $162^\circ$ , decomposing at the same time into water and its anhydride,  $\text{C}_7\text{H}_8\text{O}_3$ . The latter boils near  $275^\circ$  and by its union with water regenerates teraconic acid. Hydrobromic acid or heat and sulphuric acid cause it to change to isomeric terebic acid (a lactonic acid, see this) (*Ann.* 220, 267):—



(5) **Xeronic Acid**,  $\text{C}_8\text{H}_{12}\text{O}_4$ , or **Diethyl Fumaric Acid**,  $\text{C}_2\text{H}_5\text{C.CO}_2\text{H}$  ||  $\text{C}_2\text{H}_5\text{C.CO}_2\text{H}$  (*Ber.* 15, 1321), is very much like dimethyl fumaric acid, and when it is freed from its salts it immediately decomposes into water and the anhydride,  $\text{C}_8\text{H}_{10}\text{O}_3$ . The latter is produced in the distillation of citraconic anhydride, and is an oil which is not very soluble in water. It boils at  $242^\circ$ .

## DIBASIC ACIDS, $\text{C}_n\text{H}_{2n-6}\text{O}_4$ .

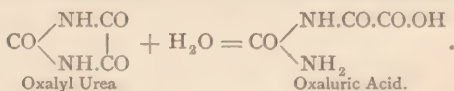
**Acetylene Dicarboxylic Acid**,  $\text{C}_4\text{H}_2\text{O}_4 = \begin{smallmatrix} \text{C.CO}_2\text{H} \\ || \\ \text{C.CO}_2\text{H} \end{smallmatrix}$ , is obtained when alcoholic potash is allowed to act upon dibrom- and isodibrom-succinic acid. It crystallizes with two molecules of water, but these escape on exposure. The anhydrous acid crystallizes with ether in thin plates, and melts with decomposition

at  $175^{\circ}$ . The acid unites with the haloid acids to form halogen fumaric acids,  $C_4H_3XO_4$  (p. 336, *Ber.*, 15, 2694). The primary *potassium salt*,  $C_4HKO_4$ , is not very soluble in water and when heated decomposes into  $CO_2$  and potassium propiolate (p. 197).

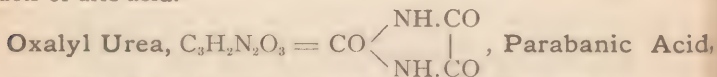
**Diallyl Malonic Acid**,  $(C_3H_5)_2C \begin{smallmatrix} \diagup CO_2H \\ \diagdown CO_2H \end{smallmatrix}$ , is obtained from malonic ester. It melts at  $133^{\circ}$ . Hydrobromic acid converts it into the corresponding *dilactone* which melts at  $106^{\circ}$  (*Ann.*, 216, 67). When heated it breaks up into  $CO_2$  and diallyl acetic acid (p. 198).

## CARBAMIDES OF THE DICARBOXYLIC ACIDS.

The urea derivatives or carbamides (ureïdes) of these acids are perfectly analogous to those of the divalent acids (p. 308). By the replacement of two hydrogen atoms in urea we obtain the true ureïdes. The alkalies convert these then into acids of the uric acid group:—



The latter decompose further into urea (also  $CO_2$  and  $NH_3$ ) and acid, whereas the ureïdes of the divalent acids yield amido-acids. Most of the carbamides were first obtained as decomposition products of uric acid.



is produced in the energetic oxidation of uric acid and alloxan (p. 344), and is obtained by evaporating a solution of uric acid in three parts of ordinary nitric acid (*Ann.*, 172, 74). It is synthetically prepared by the action of  $POCl_3$  upon a mixture of urea and oxalic acid. It is soluble in water and alcohol, but not in ether, and crystallizes in needles or prisms. Under peculiar conditions it crystallizes with one molecule of water, which it does not lose until heated to  $150^{\circ}$ . Oxalyl urea reacts acid, possesses an acidic character, as it contains two imide groups (p. 326) linked to carbonyls, and is ordinarily termed parabanic acid.

Its salts are unstable; water converts them at once into oxalates. The primary alkali salts, *e. g.*,  $C_3HKN_2O_3$ , are obtained as crystalline precipitates by the addition of potassium or sodium ethylate to an alcoholic solution of parabanic acid. Silver nitrate precipitates the crystalline *disilver salt*,  $C_3Ag_2N_2O_3$ , from solutions of the acid.

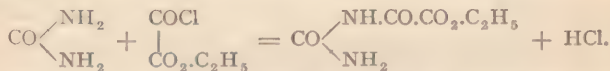
**Methyl Parabanic Acid**,  $C_3H(CH_3)N_2O_3$ , is formed by boiling methyl uric acid or methyl alloxan with nitric acid, or by treating theobromine with a chromic acid mixture. It is soluble in ether and crystallizes in prisms, which melt at  $149.5^{\circ}$ . Alkalies convert it into methyl urea and oxalic acid.

**Dimethyl Parabanic Acid**,  $C_3(CH_3)_2N_2O_3$ , **Cholestrophane**, is obtained from theine by boiling with nitric acid, chlorine water or chromic acid, or by

heating methyl iodide with silver parabanate,  $C_3Ag_2N_2O_3$ . It crystallizes in pearly laminae, melts at  $145^\circ$ , and distils at  $276^\circ$ . Alkalies decompose it into oxalic acid and dimethyl urea; the latter even yields  $CO_2$  and two molecules of  $CH_3.NH_2$ .

**Oxaluric Acid**,  $C_3H_4N_2O_4 = CO \begin{smallmatrix} \diagup NH.CO.CO_2H \\ \diagdown NH_2 \end{smallmatrix}$ . Its salts are formed by the action of bases on parabanic acid. They are not readily soluble in water, and usually separate in crystalline form. The *ammonium salt*,  $C_3H_3(NH_4)N_2O_4$ , and the *silver salt*,  $C_3H_3AgN_2O_4$ , crystallize in glistening needles. Free oxaluric acid is liberated by mineral acids from its salts as a difficultly soluble, crystalline powder. When boiled with alkalies or water it decomposes into urea and oxalic acid; heated to  $200^\circ$  with  $POCl_3$  it is again changed into parabanic acid.

The *ethyl ester*,  $C_3H_3(C_2H_5)N_2O_4$ , is formed by the action of ethyl iodide on the silver salt, and has been synthetically prepared by letting ethyl oxalyl chloride act upon urea:—

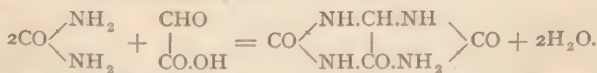


It crystallizes from warm water in thin, shining needles, which melt with decomposition at  $177^\circ$ . Ammonia and silver nitrate added to the solution of the ether precipitate silver parabanate.

*Oxaluramide*,  $C_3H_5N_3O_3 = CO \begin{smallmatrix} \diagup NH.CO.CO.NH_2 \\ \diagdown NH_2 \end{smallmatrix}$ , *Oxalan*, is produced on heating ethyl oxalurate with ammonia, and by fusing urea with ethyl oxamate,  $CO \begin{smallmatrix} \diagup NH_2 \\ \diagdown CO_2.C_2H_5 \end{smallmatrix}$ . It is a crystalline precipitate, difficultly soluble in water, and decomposes when boiled with water into urea, ammonia and oxalic acid.

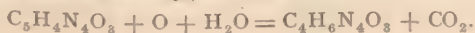
**Glyoxyl Urea**,  $C_3H_4N_2O_3 = CO \begin{smallmatrix} \diagup NH.CH.OH \\ \diagdown NH.CO \end{smallmatrix}$ , **Allanturic Acid**, is the ureide of glyoxalic acid,  $CH(OH)_2.CO_2H$ , and is obtained from allantoin on warming with baryta water or with  $PbO_2$ , and by the oxidation of glycolyl urea (hydantoïn, p. 307). It is a deliquescent, amorphous mass, insoluble in alcohol; it forms salts with one equivalent of base. When the potassium salt is boiled with water it decomposes into urea and glyoxalic acid, which is further transposed into glycollic and oxalic acids (see p. 281).

Allantoin,  $C_4H_6N_4O_3$ , is a di-ureide of glyoxalic acid. It is present in the urine of sucking calves, in the allantoinic liquid of cows, and in human urine after the ingestion of tannic acid. It is produced artificially on heating glyoxalic acid (also mesoxalic acid  $CO(CO_2H)_2$  with urea to  $100^\circ$ ):—



Pyruvil ( $C_3H_4N_4O_3$ ) is formed in a similar manner from urea and pyruvic acid.

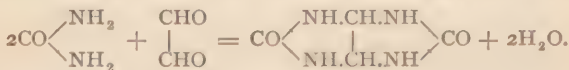
Allantoin is formed by oxidizing uric acid with  $PbO_2$ ,  $MnO_2$ , potassium ferricyanide, or with alkaline  $KMnO_4$  (*Ber.*, 7, 227):—





Allantoïn crystallizes in glistening prisms, which are slightly soluble in cold water, but readily in hot water and in alcohol. It has a neutral reaction, but dissolves in alkalis, forming salts. Ammoniacal silver nitrate precipitates the compound,  $C_4H_5AgN_4O_3$ —a white powder. When boiled with baryta water it decomposes into  $CO_2$ ,  $NH_3$ , oxalic acid and glycolyl urea (hydantoin). Sodium amalgam converts allantoïn into glyco-uril,  $C_4H_6N_4O_2$ . This consists of small octahedra, which are difficultly soluble in water. Ammoniacal silver nitrate throws down a yellow precipitate,  $C_4H_4Ag_2N_4O_2$ , from its solutions. Boiling with acids decomposes glyco-uril into urea and hydantoin, while baryta water changes it to urea and hydantoic acid.

**Acetylene Urea**,  $C_4H_6N_4O_2$ , is isomeric with glyco-uril. It separates in white needles when  $HCl$  acts on the aqueous solution of glyoxal and urea:—



**Malonyl Urea**,  $C_4H_4N_2O_3 = CO \begin{array}{c} \text{NH.CO} \\ \diagup \quad \diagdown \\ \text{NH.CO} \end{array} CH_2$ , **Barbituric Acid**, is obtained from alloxantin (p. 345) by heating it with concentrated sulphuric acid and from dibrombarbituric acid by the action of sodium amalgam. It may also be synthetically obtained by heating malonic acid and urea to  $100^\circ$  with  $POCl_3$ . It crystallizes with two molecules  $H_2O$  in large prisms from a hot solution, and when boiled with alkalis is decomposed into malonic acid and urea.

The hydrogen of  $CH_2$  in malonyl urea can be readily replaced by bromine,  $NO_2$  and the isonitroso-group. The metals in its salts are joined to carbon and may be replaced by alkyls (*Ber.*, 14, 1643, 15, 2846).

When silver nitrate is added to an ammoniacal solution of barbituric acid, a white silver salt,  $C_4H_2Ag_2N_2O_3$ , is precipitated. Methyl iodide converts this into **Dimethylbarbituric Acid**,  $CO \begin{array}{c} \text{NH.CO} \\ \diagup \quad \diagdown \\ \text{NH.CO} \end{array} C(CH_3)_2$ . This forms shining laminae, does not melt at  $200^\circ$ , and sublimes readily. Boiling alkalis decompose it into  $CO_2$ ,  $NH_3$  and dimethyl malonic acid. Its isomeride,  $\beta$ -**Dimethyl Barbituric Acid**,  $CO \begin{array}{c} \text{N(CH}_3\text{).CO} \\ \diagup \quad \diagdown \\ \text{N(CH}_3\text{).CO} \end{array} CH_2$ , is produced from malonic acid and dimethyl urea through the agency of  $POCl_3$ . It melts at  $123^\circ$ .

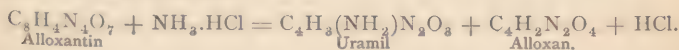
Bromine converts barbituric acid, nitro-, isonitroso-, and amido-barbituric acids into **Dibrombarbituric Acid**,  $C_4H_2Br_2N_2O_3 = CO \begin{array}{c} \text{NH.CO} \\ \diagup \quad \diagdown \\ \text{NH.CO} \end{array} CBr_2$ . This dissolves readily in hot water, in alcohol and in ether. It crystallizes in laminae or prisms. Boiling water converts it into mesoxalyl-urea (alloxan). Nascent hydrogen or  $Hl$  causes it to revert to barbituric acid and hydrogen sulphide transforms it into tartronyl-urea (dialuric acid).

**Nitrobarbituric Acid**,  $C_4H_3(NO_2)N_2O_3$ , **Dilituric Acid**, is obtained by the action of fuming nitric acid upon barbituric acid and by the oxidation of violuric acid (*Ber.*, 16, 1135). It crystallizes with  $3H_2O$  in colorless laminae or prisms, which impart a yellow color to water. It can exchange 3 hydrogen atoms for metals.

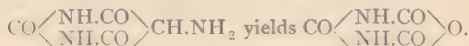
Its salts are principally those having but one equivalent of metal. They are very stable and as a general thing not decomposed by mineral acids.

**Isonitroso-barbituric Acid**,  $C_4H_2(N.OH)N_2O_3$ , **Violuric Acid**, is obtained by acting with potassium nitrite upon barbituric acid. Barium chloride precipitates a red colored salt from the solution and it is decomposed by sulphuric acid. Furthermore, it is prepared (according to the usual methods of forming isonitroso-compounds, p. 161) by the action of hydroxylamine upon alloxan. It crystallizes in yellow, rhombic octahedra with 1 molecule  $H_2O$ . It gives blue, violet and yellow colored salts with one equivalent of metal. The *potassium salt*,  $C_4H_2K(N.O)N_2O_3 + 2H_2O$ , crystallizes in dark blue prisms and dissolves in water with a violet color. Ferric acetate imparts a dark blue color to the solution. When heated with alkalis violuric acid breaks up into urea and isonitroso-malonic acid (p. 322).

**Amido-barbituric Acid**,  $C_4H_3(NH_2)N_2O_3$  (Uramil, Dialuramide, Murexan), is obtained in the reduction of nitro- and isonitroso-barbituric acid with hydriodic acid; by boiling thionuric acid with water, and by boiling alloxantin with an ammonium chloride solution:—



Alloxan remains in solution, while uramil crystallizes out. It is only slightly soluble in water, and crystallizes in colorless, shining needles, which redden on exposure. Murexide (p. 440) is produced when the solution is boiled with ammonia. Nitrous acid converts uramil into alloxan:—

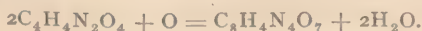


**Thionuric Acid**,  $C_4H_5N_3SO_6 = CO \begin{array}{c} \text{NH.CO} \\ \text{NH.CO} \end{array} C \begin{array}{c} \text{NH}_2 \\ \text{SO}_3H \end{array}$ , **sulphaminbarbituric acid**, is obtained by heating isonitrosobarbituric acid or alloxan with ammonium sulphite. Its *ammonium salt*,  $C_4H_4(NH_4)N_3SO_6 + H_2O$ , is made by boiling alloxan with sulphurous acid and ammonia. It forms bright scales. Free thionuric acid is obtained by acting on the lead salt with hydrogen sulphide. It is a readily soluble crystalline mass. It reduces ammoniacal silver solutions, and when boiled with water breaks up into sulphuric acid and uramil.

**Tartronyl Urea**,  $C_4H_4N_2O_4 = CO \begin{array}{c} \text{NH.CO} \\ \text{NH.CO} \end{array} \text{CH.OH}$ , **dialuric acid**, the ureide of tartronic acid  $CH(OH)(CO_2H)_2$ , is formed by the reduction of mesoxalyl urea (alloxan) with zinc and hydrochloric acid, and from dibrombarbituric acid by the action of  $H_2S$ . On adding hydrocyanic acid and potassium carbonate to an aqueous solution of alloxan, potassium dialurate separates but potassium oxalurate remains dissolved:—



Dialuric acid crystallizes in needles or prisms, has a very acid reaction and affords salts with 1 and 2 equivalents of the metals. It becomes red in color in the air, absorbs oxygen and passes over into alloxantin:—



**Mesoxalyl Urea**,  $C_4H_2N_2O_4 = CO \begin{smallmatrix} \text{NH.CO} \\ \text{NH.CO} \end{smallmatrix} CO$ , **Alloxan**,

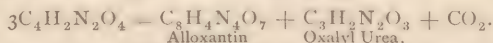
the ureide of mesoxalic acid, is produced by the careful oxidation of uric acid, or alloxantin with nitric acid or chlorine and bromine.

*Preparation.*—Add uric acid gradually to cold nitric acid of specific gravity 1.4, as long as a reaction occurs. Then let the whole stand for some time. The separated, crystalline mass of alloxan is drained upon an asbestos filter, warmed upon a water bath to expel all nitric acid, and then recrystallized from water; alloxantin remains in the mother-liquor.

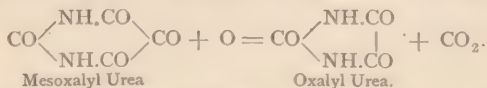
Moisten alloxantin with concentrated nitric acid (sp. gr. 1.46), let stand until it has been completely changed to alloxan (a sample should dissolve readily in cold water), and then purify the latter as already described.

Alloxan crystallizes from warm water in long, shining, rhombic prisms, with 4 molecules of  $H_2O$ . When exposed to the air they effloresce with separation of 3  $H_2O$ . The last molecule of water is intimately combined (p. 323), as in mesoxalic acid and does not escape until heated to  $150^\circ$ . Small, stable crystals, with 1  $H_2O$  separate out from hot solutions. Alloxan is easily soluble in water, has a very acid reaction and possesses a disagreeable taste. The solution placed on the skin slowly stains it a purple red. Ferrous salts impart a deep indigo blue color to the solution. When hydrocyanic acid and ammonia are added to the aqueous solution the alloxan decomposes into  $CO_2$ , dialuric acid and oxaluramide (p. 341), which separates as a white precipitate (reaction for detection of alloxan).

The primary alkali sulphites unite with alloxan just as they do with mesoxalic acid, and we obtain crystalline compounds *e. g.*,  $C_4H_2N_2O_4 \cdot SO_3KH + H_2O$ . Pure alloxan can be preserved without undergoing decomposition, but in the presence of even minute quantities of nitric acid it is converted into alloxantin. Alkalies, lime or baryta water change it to alloxanic acid, even when acting in the cold. Its aqueous solution undergoes a gradual decomposition (more rapid on heating) into alloxantin, parabanic acid and  $CO_2$  :—



Boiling dilute nitric acid oxidizes alloxan to parabanic acid (oxalyl urea) and  $CO_2$  :—

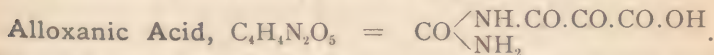


The mesoxalic acid residue, like the free acid (p. 323), splits off a CO-group, readily forming oxalyl.

Reducing agents, like hydriodic acid, change alloxan, in the cold, to alloxantin, on warming, however, into tartronyl urea (dialuric acid).

**Methyl Alloxan**,  $C_4H(CH_3)N_2O_4$ , is produced by the oxidation of methyl uric acid. Alkalies convert it at once into methyl alloxanic acid. Nitric acid changes it to methyl parabanic acid (p. 340).

**Dimethyl Alloxan**,  $\text{CO}(\text{N}.\text{CH}_3)_2\text{C}_3\text{O}_3$ , is produced when aqueous chlorine (hydrochloric acid and  $\text{KClO}_3$ ) acts on theïne, and by the careful oxidation of tetramethyl alloxantin with nitric acid. When the solution is concentrated dimethyl alloxan remains as a non-crystallizable syrup. It manifests all the reactions of alloxan.  $\text{H}_2\text{S}$  reduces it to tetramethyl alloxantin (see below). By energetic oxidation it yields dimethyl oxalyl urea (p. 340).



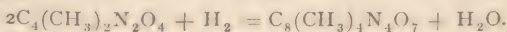
When the alkalies act on alloxan the latter absorbs water and passes into the acid. If baryta water be added to a warm solution of alloxan, as long as the precipitate which forms continues to dissolve, barium alloxanate,  $\text{C}_4\text{H}_2\text{BaN}_2\text{O}_5 + 4\text{H}_2\text{O}$ , will separate out in needles when the solution cools. To obtain the free acid decompose the barium salt with sulphuric acid and evaporate at a temperature of  $30-40^\circ$ . A mass of crystals is obtained by this means. Water dissolves them easily. Alloxanic acid shows a very acid reaction, dissolves zinc, and is indeed a dibasic acid, inasmuch as both the hydrogen of carboxyl and of the imide group can be exchanged for metals (p. 326). When the salts are boiled with water they decompose into urea and mesoxalates.

By the union of two molecules of the ureïdes of the dicarboxylic acids we get the compounds oxalantin, alloxantin, and hydurilic and purpuric acids. These are termed di-ureïdes.

**Oxalantin**,  $\text{C}_6\text{H}_6\text{N}_4\text{O}_6$ , Leucoturic acid, is obtained by the action of zinc and hydrochloric acid upon oxalyl urea:  $-2\text{C}_3\text{H}_2\text{N}_2\text{O}_3 + \text{H}_2 = \text{C}_6\text{H}_6\text{N}_4\text{O}_6$ .  $\text{H}_2\text{S}$  will separate it from the zinc salt. It forms crystalline crusts which dissolve with difficulty in water, and it also reduces ammoniacal solutions of both silver and mercury.

**Alloxantin**,  $\text{C}_8\text{H}_4\text{N}_4\text{O}_7$ , is obtained by reducing alloxan with  $\text{SnCl}_2$ , zinc and hydrochloric acid, or  $\text{H}_2\text{S}$  in the cold:  $-2\text{C}_4\text{H}_2\text{N}_2\text{O}_4 + \text{H}_2 = \text{C}_8\text{H}_4\text{N}_4\text{O}_7 + \text{H}_2\text{O}$ ; or by mixing solutions of alloxan and dialuric acid:  $\text{C}_4\text{H}_2\text{N}_2\text{O}_4 + \text{C}_4\text{H}_4\text{N}_2\text{O}_4 = \text{C}_8\text{H}_4\text{N}_4\text{O}_7 + \text{H}_2\text{O}$ . Most readily prepared by warming uric acid with dilute nitric acid (*Ann.*, 147, 367). It crystallizes from hot  $\text{H}_2\text{O}$  in small, hard prisms with  $3\text{H}_2\text{O}$  and turns red in air containing ammonia. Its solution has an acid reaction; ferric chloride and ammonia give it a deep blue color, and baryta water produces a violet precipitate, which on boiling is converted into a mixture of barium alloxanate and dialurate.

**Tetramethyl Alloxantin**,  $\text{C}_8(\text{CH}_3)_4\text{N}_4\text{O}_7 = \text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_7$ , **Amalic Acid**, is formed by the action of nitric acid or chlorine water upon theïne, or better, by the reduction of dimethyl alloxan (see above) with hydrogen sulphide (*Ann.*, 215, 258):—



It consists of colorless, difficultly soluble crystals, which impart a red color to the skin; alkalies and baryta water give it a violet-blue color. When carefully oxidized by nitric acid, or by the action of chlorine (*Ann.*, 221, 330) it is again altered to dimethyl alloxan; more energetic reaction produces dimethyl parabanic acid.

**Hydurilic Acid**,  $\text{C}_8\text{H}_6\text{N}_4\text{O}_6$ . The ammonium salt is formed on boiling alloxantin with dilute sulphuric acid; by heating dialuric acid with glycerol to



150°; and also on heating aqueous alloxan or alloxantin to 170°. The free acid is obtained by decomposing the copper salt with hydrochloric acid. It crystallizes from hot water in little prisms having  $2\text{H}_2\text{O}$ , and is a dibasic acid. Ferric chloride imparts a dark green color to the solution of the acid or its salts. Ordinary nitric acid decomposes hydruilic acid into nitro- and nitroso-barbituric acid; fuming nitric acid forms alloxan.

**Purpuric Acid**,  $\text{C}_8\text{H}_5\text{N}_5\text{O}_6$ , is not known in the free state, because as soon as it is liberated from its salts by mineral acids it immediately decomposes into alloxan and uramil. The ammonium salt,  $\text{C}_8\text{H}_4(\text{NH}_4)\text{N}_5\text{O}_6 + \text{H}_2\text{O}$ , is the dye-stuff *murexide*. This is formed by heating alloxantin to 100° in ammonia gas; by mixing ammoniacal solutions of alloxan and uramil:—

$\text{C}_4\text{H}_2\text{N}_2\text{O}_4 + \text{C}_4\text{H}_5\text{N}_3\text{O}_3 + \text{NH}_3 = \text{C}_8\text{H}_4(\text{NH}_4)\text{N}_5\text{O}_6 + \text{H}_2\text{O}$ ;  
and by evaporating uric acid with dilute nitric acid and pouring ammonia over the residue (murexide reaction). It is most readily obtained from uramil (p. 343). Dissolve 4 parts of the latter in dilute ammonium hydrate, add 3 parts of mercuric oxide and heat to boiling, when mercury will separate and the solution assume a dark-red color:—



Murexide separates from the solution on cooling. It forms four-sided plates or prisms with one molecule of  $\text{H}_2\text{O}$ , and has a gold-green color. It dissolves in water with a purple-red color, but is insoluble in alcohol and ether. It dissolves with a dark blue color in potash; on boiling  $\text{NH}_3$  is disengaged and the solution decolorized.

**Uric Acid**,  $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ , occurs in the juice of the muscles, in the blood and in the urine, especially of the carnivoræ, the herbivoræ separating hippuric acid; also, in the excrements of birds, reptiles and insects. When urine is exposed for awhile to the air, uric acid separates; this also occurs in the organism (formation of gravel and joint concretions) in certain abnormal conditions.

Uric acid is prepared artificially by heating glycocoll with urea (10 parts) to 200–230° (*Ber.*, 15, 2678).

Uric acid is best prepared from guano and the excrements of reptiles. Guano is boiled with a hot borax solution (1 part borax in 120 parts  $\text{H}_2\text{O}$ ) and the uric acid precipitated from the filtrate by hydrochloric acid. Or after removing the phosphates from guano by means of dilute hydrochloric acid, it is dissolved in concentrated sulphuric acid (in equal weight), and the uric acid precipitated by pouring the solution into water (12–15 vols). To obtain the acid pure, it is dissolved in caustic potash and carbon dioxide conducted into the liquid, when potassium urate will be precipitated; hydrochloric acid sets free the uric acid.

The excrements of reptiles (ammonium urate) are boiled with dilute potassium or sodium hydrate until the odor of ammonia is no longer perceptible, the hot solution filtered and the filtrate poured into dilute hydrochloric acid.

Uric acid is precipitated as a shining, white powder, from solutions of its salts. It is odorless and tasteless, insoluble in alcohol and ether, and difficultly soluble in water; 1 part requires 15,000 parts water of 20° for its solution, and 1800 parts at 100°. Its solubility is increased by the presence of salts like sodium phosphate and borate. Water precipitates it from its solution in con-

concentrated sulphuric acid. On evaporating uric acid to dryness with nitric acid, we obtain a yellow residue, which assumes a purple-red color if moistened with ammonia, or violet with caustic potash or soda (murexide reaction, p. 346). Heat decomposes uric acid into  $\text{NH}_3$ ,  $\text{CO}_2$ , urea and cyanuric acid.

Uric acid acts like a weak dibasic acid, forming chiefly, however, salts containing but one equivalent of metal. The secondary alkali salts are obtained by dissolving the primary salts or the free acid in the hydrates of potassium and sodium; they show a very alkaline reaction, and are changed to the primary form by  $\text{CO}_2$  and water. When  $\text{CO}_2$  is conducted through the alkaline solution, the primary salts are precipitated. Uric acid only affords primary salts with the alkaline carbonates.

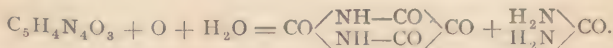
The *dipotassium salt*,  $\text{C}_5\text{H}_2\text{K}_2\text{N}_4\text{O}_3$ , separates in needles when its solution is evaporated. It dissolves easily in potash and in 40 parts  $\text{H}_2\text{O}$  at ordinary temperatures. The *primary salt*,  $\text{C}_5\text{H}_3\text{KN}_4\text{O}_3$ , is precipitated from solutions of the dipotassium salt as a jelly, which soon becomes granular and dissolves in 800 parts  $\text{H}_2\text{O}$  at  $20^\circ$ . The *primary sodium salt* is more insoluble. The *primary ammonium salt*,  $\text{C}_5\text{H}_3(\text{NH}_4)\text{N}_4\text{O}_3$ , is precipitated as a difficultly soluble powder, by ammonium chloride, from the solutions of the other salts.

**Methyl Uric Acid**,  $\text{C}_5\text{H}_3(\text{CH}_3)\text{N}_4\text{O}_3$ , is obtained by heating primary lead urate with methyl iodide and ether to  $160^\circ$ . It consists of small needles, which are rather insoluble in water. When heated with concentrated hydrochloric acid to  $170^\circ$  it decomposes into  $\text{NH}_3$ ,  $\text{CO}_2$ , methylamine and glycochol (*Ber.*, 17, 330).

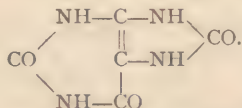
**Dimethyl Uric Acid**,  $\text{C}_5\text{H}_2(\text{CH}_3)_2\text{N}_4\text{O}_3$ , obtained from the secondary lead salt, crystallizes with one molecule  $\text{H}_2\text{O}$ , which is not expelled until heated to  $160^\circ$ . It yields the same decomposition products as the preceding (2 molecules methylamine). Both acids are capable of forming primary and secondary salts, which are perfectly analogous to those of uric acid.

Careful oxidation converts dimethyl uric acid (analogous to uric acid) into methyl alloxan and methyl urea.

When uric acid is carefully oxidized, either with cold nitric acid or with potassium chlorate and hydrochloric acid, it yields mesoxalyl urea and urea:—



Its structure is approximately represented by the formula;—



The presence of four imide groups explains how it and also dimethyl uric acid are capable of affording salt-like compounds with 1 and 2 equivalents of the metals.



**Xanthine**,  $C_5H_4N_4O_2$ , occurs in slight amounts in many animal secretions, in the blood, in urine, in the liver and in some forms of calculi. It results from the action of nitrous acid upon guanine (*Ann.*, 215, 309). It is a white, amorphous mass, somewhat soluble in boiling water, and combines with both acids and bases. It is readily soluble in boiling ammonia; silver nitrate precipitates  $C_5H_2Ag_2N_4O_2 + H_2O$  from its solution. The corresponding lead compound yields theobromine (dimethyl xanthine) when heated to  $100^\circ$  with methyl iodide. When xanthine (analogous to caffeïne, p. 348) is warmed with potassium chlorate and hydrochloric acid it splits into alloxan and urea.

**Sarcine**,  $C_5H_4N_4O$ , Hypoxanthine, is a constant attendant of xanthine in the animal organism, and is distinguished principally by the difficult solubility of its hydrochloride. It consists of needles not very soluble in water, but dissolved by alkalis and acids. Silver nitrate precipitates the compound  $C_5H_2Ag_2N_4O + H_2O$  from ammoniacal solutions.

**Carnine**,  $C_7H_8N_4O + H_2O$ , has been found in the extract of beef. It is a powder, rather easily soluble in water, and forms a crystalline compound with hydrochloric acid. Bromine water or nitric acid converts carnine into sarcine.

**Theobromine**,  $C_7H_8N_4O_2 = C_5H_2(CH_3)_2N_4O$ , dimethyl xanthine, occurs in cocoa-beans (from *Theobroma Cacao*) and is prepared by introducing methyl into xanthine (see above).

Divided cocoa-beans are boiled with water, tannic acid and other substances precipitated by basic lead acetate, and  $H_2S$  conducted into the filtrate to remove excess of lead. The solution is then evaporated to dryness and the theobromine extracted from the residue with alcohol.

Theobromine is a crystalline powder with a bitter taste and dissolves with difficulty in hot water and alcohol, but rather easily in ammonium hydrate. It sublimes (about  $290^\circ$ ) without decomposition, when it is carefully heated. It has a neutral reaction, but yields salts on dissolving in acids; much water will decompose these. Silver nitrate precipitates the compound,  $C_7H_7AgN_4O_2$ , in crystalline form from the ammoniacal solution after protracted heating. When this salt is heated with methyl iodide it yields methyl theobromine,  $C_7H_7(CH_3)N_4O_2$ , *i. e.*, caffeïne.

**Caffeïne**, **Theïne**,  $C_8H_{10}N_4O_2$ , methyl theobromine, trimethyl xanthine (p. 348), occurs in the leaves and beans of the coffee tree ( $\frac{1}{2}\%$ ), in tea (2–4%), in Paraguay tea (from *Ilex paraguayensis*), and in guarana (about 5%)—the roasted pulp of the fruit of *Paullinia sorbilis*. The caffeïne is procured from these sources, just as theobromine is obtained. It is also found in minute quantities in cocoa.

Caffeïne affords long, silky needles with 1 molecule of water; they are only slightly soluble in cold water, and alcohol. At  $100^\circ$  it loses its water, melts at  $225^\circ$  and sublimes at higher temperatures.

It possesses a feeble bitter taste and yields salts with the strong mineral acids; water readily decomposes them. On evaporating a solution of chlorine water containing traces of caffeïne we get a reddish-brown spot, which acquires a beautiful violet-red color when dissolved in ammonia water.



Sodium hydroxide converts theine into caffeidine carboxylic acid,  $C_7H_{11}N_4O \cdot CO_2H$ , which readily decomposes into  $CO_2$  and caffeidine,  $C_7H_{12}N_4O$  (*Ber.*, 16, 2309). The latter is also obtained when caffeine is boiled with baryta water; it is a readily soluble, strong base and decomposes on protracted boiling into  $NH_3$ , methylamine, formic acid and methyl glyccoll. For other caffeine derivatives (apocaffeine, caffuric acid, caffolin) see *Ann.*, 215, 261.

Chlorine water breaks caffeine up into dimethyl alloxan and methylurea (p. 348). By energetic action of chlorine, dimethyl parabanic acid is produced. This is also formed in the oxidation of theine with chromic acid, while theobromine yields methyl parabanic acid.

### TRIVALENT COMPOUNDS.

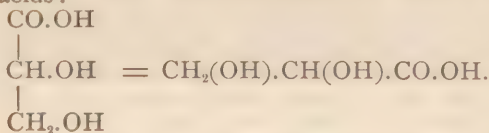
The trivalent compounds are derived from the hydrocarbons in the same manner as the mono- and divalent; three hydrogen atoms are replaced by three monovalent groups. Their methods of formation and transposition are also perfectly analogous to those of the mono- and di-derivatives.

When three hydroxyl groups are introduced **trivalent (trihydric) alcohols** are formed:



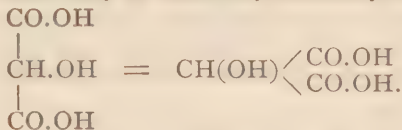
Glycerol.

By the conversion of one primary alcoholic group,  $CH_2.OH$ , into carboxyl we obtain the *trivalent monobasic acids*, in which two alcoholic hydroxyls remain, hence they can be termed dioxy-mono-carboxylic acids:



Trivalent Monobasic Acid,  
Glyceric Acid or Dioxypropionic Acid.

The *trivalent dibasic acids* contain two carboxyl groups and one alcohol group; hence may be called oxy-dicarboxylic acids:—



Trivalent Dibasic Acid  
Tartronic or Oxymalonic Acid.

The *tribasic acids*, finally, contain three carboxyl groups:—

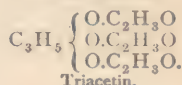
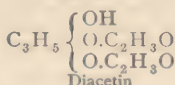
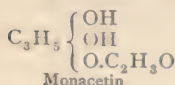
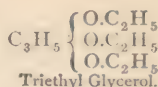
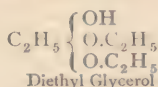
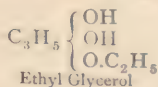


Tribasic or Tricarboxylic Acid.

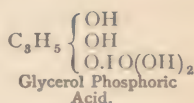
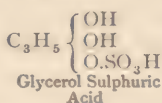
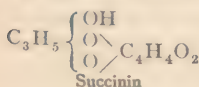
Many derivatives attach themselves to the trivalent alcohols and acids.

## TRIVALENT (TRIHYDRIC) ALCOHOLS.

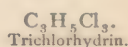
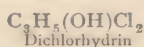
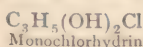
In these, three hydrogen atoms can be replaced by alcohol or acid residues, forming ethers and esters:—



The polybasic acids afford similar esters:—



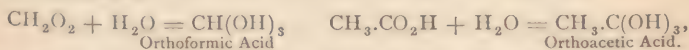
The esters of the haloid acids, like



may be viewed as substitution products of the di- and trivalent alcohols.

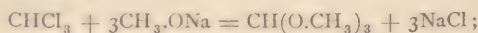
Glycerol,  $\text{C}_3\text{H}_5(\text{OH})_3$ , is the first member of the trihydric alcohols. Lower homologues cannot exist, because in general one carbon atom is capable of linking only one hydroxyl group in such a manner that the hydrogen in it will be exchangeable in any further replacement. Ethers and esters of trihydroxyl compounds with one and two carbon atoms do exist (p. 256).

Certain hydrates of the fatty acids, having constant boiling points at times (see formic acid) may be considered as trihydroxyl derivatives; hence, they have been called ortho-acids:

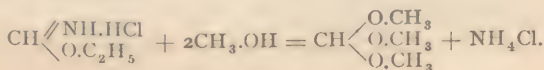


just as the hydrate of nitric acid,  $\text{NO}_3\text{H} + \text{H}_2\text{O} = \text{NO}(\text{OH})_3$ , is termed ortho-nitric acid.

We get the esters of orthoformic acid by heating chloroform with an alcoholic solution of sodium alcoholates:—



or by the union of form-imido-ethers (p. 249) with alcohols, resulting in mixed esters (*Ber.*, 16, 1645):—



When sodium mercaptides act on chloroform, we obtain esters of orthothioformic acid, *e. g.*,  $\text{CH}(\text{S.CH}_3)_3$ .

**Methyl Orthoformic Ester**,  $\text{CH}(\text{O.CH}_3)_3$ , boils at  $102^\circ$ , and has a specific gravity 0.974 at  $23^\circ$ . The **Triethyl Ester**,  $\text{CH}(\text{O.C}_2\text{H}_5)_3$ , is an aromatic-smelling liquid, insoluble in water, and boiling at  $146^\circ$ ; sp. gr. 0.896. It decomposes into ethyl formic and ethyl acetic esters, when heated with glacial acetic acid.

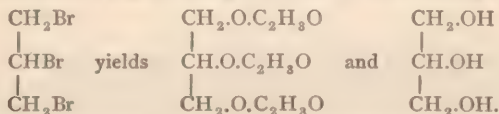
**Methine Trisulphonic Acid**,  $\text{CH}(\text{SO}_3\text{H})_3$ , is obtained by heating chloropicrin,  $\text{CCl}_3(\text{NO})_2$ , with a concentrated aqueous solution of sodium sulphite, or by heating calcium methyl sulphonate (p. 120) with fuming sulphuric acid. This acid, like all sulphonic acids, is very stable and is not affected by boiling alkalis.

**Ethyl Ortho-acetic Ester**,  $\text{CH}_3.\text{C}(\text{O.C}_2\text{H}_5)_3$ , triethyl acetyl ester, is obtained by heating  $\alpha$ -trichlorethane,  $\text{CH}_3.\text{CCl}_3$ , with an ethereal solution of sodium ethylate. It boils at  $142^\circ$ , and when heated with water to  $120^\circ$  breaks up into acetic acid and alcohol.

Isomeric with the preceding is

**Triethyl Ethenyl Ester**,  $\begin{array}{c} \text{CH}_2.\text{O.C}_2\text{H}_5 \\ | \\ \text{CH}(\text{O.C}_2\text{H}_5)_2 \end{array}$ , which is obtained from chloroacetal,  $\text{CH}_2\text{Cl.CH}(\text{O.C}_2\text{H}_5)_2$  (p. 259). It boils at  $168^\circ$ .

**Glycerol**,  $\text{C}_3\text{H}_8\text{O}_3 = \text{C}_3\text{H}_5(\text{OH})_3$ , glycerine, is produced in small quantities in the alcoholic fermentation of sugar. It is prepared exclusively from the fats and oils, which are glycerol esters of the fatty acids (p. 357). When the fats are saponified by bases or sulphuric acid, they decompose, like all esters, into fatty acids and the alcohol—glycerol. It is obtained synthetically from allyl tribromide (p. 76) by converting the latter, with silver acetate, into glycerol acetate and saponifying this ester with boiling alkalis:—



Glycerol is similarly formed from glyceryl trichloride (from propylene chloride) by heating it with water to  $170^\circ$ .

In preparing glycerol from fats (chiefly olive oil), the latter were formerly saponified by boiling them with lead oxide and water. The aqueous solution of glycerol was separated from the insoluble lead salt of the fatty acids (lead plaster, p. 186), the dissolved lead precipitated by hydrogen sulphide and the filtrate concentrated by evaporation.

At present glycerol is produced in large quantities in the manufacture of stearic acid; the fats are saponified by means of superheated steam, converting them directly into glycerol and fatty acids. In most stearic acid factories sulphuric acid is employed for the saponification. The glycerol then exists as glycerol-sulphuric acid (p. 353) in the aqueous solution. To liberate the glycerol the solution is boiled with lime, the gypsum filtered off, the liquid concentrated and

distilled with superheated steam. In order to obtain a pure product the glycerol is again distilled under diminished pressure.

Anhydrous glycerol is a thick, colorless syrup, of specific gravity 1.27. Under certain conditions it solidifies to a white, crystalline mass, which melts at  $+17^{\circ}$ . Under ordinary atmospheric pressure it boils at  $290^{\circ}$  (cor.) without decomposition; under diminished pressure or with superheated steam it distils entirely unaltered. It has a pure, sweet taste, hence the name glycerol. It absorbs water very energetically when exposed and mixes in every proportion with water and alcohol, but is insoluble in ether. It dissolves the alkalis, alkaline earths and many metallic oxides, forming with them, in all probability, metallic compounds similar to the alcoholates (p. 96).

When glycerol is distilled with dehydrating substances, like sulphuric acid and phosphorus pentoxide, it decomposes into water and acrolein (p. 158). It sustains a similar and partial decomposition when it is distilled alone. When fused with caustic potash it evolves hydrogen and yields acetic and formic acids. Platinum black or dilute nitric acid oxidizes it to glyceric and tartronic acids, but under energetic oxidation the products are oxalic acid, glycollic acid, glyoxylic and other acids. Phosphorus iodide or hydriodic acid converts it into allyl iodide, isopropyl iodide and propylene (p. 68). In the presence of yeast at  $20-30^{\circ}$  it ferments, forming propionic acid.

**Nitroglycerine**, Trinitrin, glycerol nitric ester,  $C_3H_5(O.NO_2)_3$  (p. 257), is produced by the action of a mixture of sulphuric and nitric acids upon glycerol. The latter is added, drop by drop, to a well cooled mixture of equal volumes of concentrated nitric and sulphuric acids, as long as it dissolves; the solution is then poured into water and the separated, heavy oil (nitroglycerine) is washed with water and dried by means of calcium chloride.

Nitroglycerine is a colorless oil, of sp. gr. 1.6, and becomes crystalline at  $-20^{\circ}$ . It has a sweet taste and is poisonous when taken inwardly. It is insoluble in water, difficultly soluble in cold alcohol, but easily soluble in wood spirit and ether. Heated quickly or upon percussion it explodes very violently (*Nobel's explosive oil*); mixed with *kieselguhr* it forms *dynamite*.

Alkalies convert nitroglycerine into glycerol and nitric acid; ammonium sulphide also regenerates glycerol. Both reactions prove that nitroglycerine is not a nitro-compound, but a nitric acid ester.

**Glycerol-Nitrite**,  $C_3H_5(O.NO)_3$ , is formed by the action of  $N_2O_3$  upon glycerol. It boils at  $150^{\circ}$  with partial decomposition. Water breaks it up with evolution of oxides of nitrogen. Its isomeride, **Trinitropropane**,  $C_3H_5(NO_2)_3$  is obtained from glyceryl bromide by the action of silver nitrite (p. 78). It is an oil, boiling at  $200^{\circ}$ .

**Glycerol Sulphuric Acid**,  $C_3H_5 \left\{ \begin{smallmatrix} (OH)_2 \\ O.SO_3H \end{smallmatrix} \right.$ , is formed by mixing 1 part glycerol with 1 part of sulphuric acid. The free acid decomposes when its aqueous solution is heated. Its salts are readily soluble; the calcium salt is crystalline.

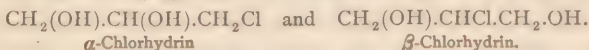
**Glycerol-Phosphoric Acid**,  $C_3H_5 \left\{ \begin{smallmatrix} (OH)_2 \\ O.PO_3H_2 \end{smallmatrix} \right.$ , occurs combined with the fatty acids and choline as lecithin (see this) in the yolk of eggs, in the brain, in



the bile, and in the nervous tissue. It is produced on mixing glycerol with metaphosphoric acid. The free acid is a stiff syrup, which decomposes into glycerol and phosphoric acid when it is heated with water. It yields easily soluble salts with two equivalents of metal. The calcium salt is more insoluble in hot than in cold water; on boiling its solution it deposits in glistening leaflets.

### HALOID ESTERS OF GLYCEROL (PROPENYL SALTS).

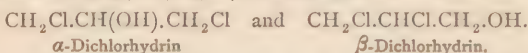
*Monochlorhydrins*,  $C_3H_5(OH)_2Cl$ . There are two possible isomerides:—



**$\alpha$ -Chlorhydrin** is produced, together with a little of the  $\beta$ -variety, on heating glycerol and hydrochloric acid to  $100^\circ$ . It is best prepared by heating epichlorhydrin (p. 355) with water (1 molecule) to  $120^\circ$  (*Ber.*, 13, 457). It is a thick liquid, soluble in water, alcohol and ether; it boils with partial decomposition at  $215^\circ$ . Sodium amalgam converts it into propylene glycol; and when oxidized it becomes  $\beta$ -chlorlactic acid.

**$\beta$ -Chlorhydrin** is obtained from allyl alcohol by the addition of hypochlorous acid. It boils at  $230^\circ$ .

*Dichlorhydrins*,  $C_3H_5(OH)Cl_2$  (*Dichlorpropyl Alcohols*):—



**$\alpha$ -Dichlorhydrin** is produced by the action of hydrochloric acid or chloride of sulphur upon glycerol. It is obtained perfectly pure by shaking epichlorhydrin (p. 355) with concentrated hydrochloric acid.

*Preparation.*—Saturate a mixture of glycerol (3 parts) and glacial acetic acid (2 parts) with hydrochloric acid gas, accelerating the absorption toward the end by applying heat. The strongly fuming product is washed with a soda solution and the separated oil distilled. The portion going over from  $160$ – $200^\circ$  contains  $\alpha$  dichlorhydrin and acetochlorhydrin. These are difficult to separate (*Ann.*, 208, 361). Therefore, epichlorhydrin is first prepared from the crude dichlorhydrin by adding pulverized caustic soda gradually to the portion which distils at  $170$ – $180^\circ$ , so that the temperature does not exceed  $130^\circ$ . The resulting epichlorhydrin is distilled off (*Ber.*, 10, 557) and changed to  $\alpha$ -dichlorhydrin by shaking with concentrated hydrochloric acid.

**$\alpha$ -Dichlorhydrin** is a liquid, with ethereal odor, of sp. gr. 1.367 at  $19^\circ$ , and boils at  $171$ – $172^\circ$ . It is not very soluble in water (in 9 parts at  $19^\circ$ ), but dissolves readily in alcohol and ether. When heated with hydriodic acid it becomes isopropyl iodide; sodium amalgam produces isopropyl alcohol. Chromic acid oxidizes it to  $\beta$ -dichloracetone (p. 163) and chloracetic acid.

When sodium acts on an ethereal solution of  $\alpha$ -dichlorhydrin, we do not get trimethylene alcohol,  $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} \rangle CH.OH$ , but allyl alcohol as a result of molecular transposition.

**$\beta$ -Dichlorhydrin**,  $\text{CH}_2\text{Cl}.\text{CHCl}.\text{CH}_2.\text{OH}$ , obtained by adding chlorine to allyl alcohol or hypochlorous acid to allyl chloride, boils at  $182-183^\circ$ ; its sp. gr. = 1.379 at  $0^\circ$ . Sodium converts it into allyl alcohol. Fuming nitric acid oxidizes it to  $\alpha,\beta$ -dichlorpropionic acid.

Both dichlorhydrins are changed to epichlorhydrin by the alkalies.

**Trichlorhydrin**,  $\text{C}_3\text{H}_5\text{Cl}_3$ , is made by the action of  $\text{PCl}_5$  upon both dichlorhydrins, and has already been described, p. 76, as glyceryl trichloride.

**$\alpha$ -Monobromhydrin**,  $\text{C}_3\text{H}_5(\text{OH})_2\text{Br}$ , is formed when  $\text{HBr}$  acts on glycerol. It is an oily liquid, which boils at  $180^\circ$  under diminished pressure.

**$\alpha$ -Dibromhydrin**,  $\text{CH}_2\text{Br}.\text{CH}(\text{OH}).\text{CH}_2\text{Br}$ , is an ethereal-smelling liquid, which boils at  $219^\circ$ ; its sp. gr. at  $18^\circ$  is 2.11.

**$\beta$ -Dibromhydrin**,  $\text{CH}_2\text{Br}.\text{CHBr}.\text{CH}_2.\text{OH}$ , boils at  $212-214^\circ$ .

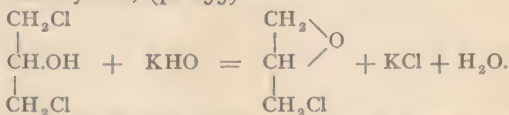
**Tribromhydrin**,  $\text{C}_3\text{H}_5\text{Br}_3$ , is described on p. 76.  **$\alpha$ -Monoiodhydrin**,  $\text{C}_3\text{H}_5(\text{OH})_2\text{I}$ , is obtained by heating glycerol and  $\text{HI}$  to  $100^\circ$ ; it is a thick liquid of sp. gr. 1.783.

**$\alpha$ -Di-iodhydrin**,  $\text{CH}_2\text{I}.\text{CH}(\text{OH}).\text{CH}_2\text{I}$ , is prepared by heating  $\alpha$ -dichlorhydrin with aqueous potassium iodide. A thick oil of specific gravity 2.4 and solidifying at  $-15^\circ$ .

## GLYCID E COMPOUNDS.

By this designation we understand certain compounds formed from glycerol derivatives by the exit of  $\text{H}_2\text{O}$  or  $\text{HCl}$ . These are again readily converted into glycerol derivatives.

**Epichlorhydrin**,  $\text{C}_3\text{H}_5\text{OCl}$ , is isomeric with monochloracetone, and is obtained from both dichlorhydrins (p. 354) by the action of caustic potash or soda (analogous to the formation of ethylene oxide from glycolchlorhydrin, (p. 255):—

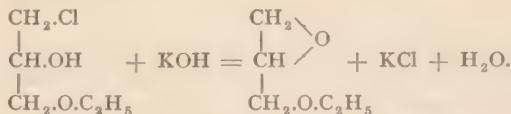


It is a very mobile liquid, insoluble in water and boils at  $117^\circ$ . Its sp. gravity at  $0^\circ$  is 1.203. Its odor resembles that of chloroform, and its taste is sweetish and burning. It forms  $\alpha$ -dichlorhydrin with concentrated hydrochloric acid.  $\text{PCl}_5$  converts it into trichlorhydrin. Continued heating with water to  $180^\circ$  changes it to monochlorhydrin. Concentrated nitric acid oxidizes it to  $\beta$ -chlorlactic acid.

Like ethylene oxide, epichlorhydrin combines with sodium bisulphite, and with  $\text{CNH}$  to the oxycyanide,  $\text{C}_3\text{H}_5\text{Cl} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{CN} \end{smallmatrix}$ . Hydrochloric acid changes the latter to

an acid. **Epicyanhydrin**,  $C_3H_5O.CN$ , is formed when CNK acts on epichlorhydrin. Brilliant crystals which fuse at  $162.3^\circ$  and become **Epihydrin-carboxylic Acid**,  $C_3H_5O.CO_2H$ , under the influence of HCl (*Ber.*, 15, 2586).

The ethers of chlorhydrin, like  $C_3H_5Cl(OH).O.C_2H_5$ , are produced on warming epichlorhydrin with alcohols. When they are distilled with caustic potash *glycide ethers* appear:—



**Ethyl Glycide Ether**,  $C_3H_5O.O.C_2H_5$  (Epiethylin), boils at  $130^\circ$ ; **amyl glycide ether**,  $C_3H_5O.O.C_5H_{11}$ , at  $188^\circ$ .

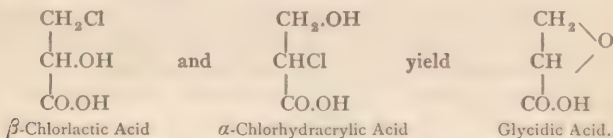
**Acetic Glycide Ester**,  $C_3H_5O.O.C_2H_3O$ , is produced by heating epichlorhydrin with anhydrous potassium acetate. It boils at  $168-169^\circ$ .

**Glycide Alcohol**,  $C_3H_5O.OH$ , is formed by the decomposition of its acetate by caustic soda or baryta. It boils near  $162^\circ$  and is miscible with water, alcohol and ether; its specific gravity is 1.165 at  $0^\circ$ . It reduces ammoniacal silver solutions at ordinary temperatures.

When epichlorhydrin is heated with sodium acetate and absolute alcohol the reaction proceeds as follows:—

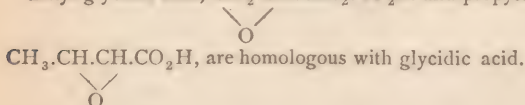
$C_3H_5OCl + C_2H_3O_2Na + C_2H_5.OH = C_3H_5O.OH + C_2H_3O_2.C_2H_5 + NaCl$ . The glycide formed at first condenses to polyglycides, chiefly diglycide ( $C_3H_5O.OH$ )<sub>2</sub>, which boils at  $250^\circ$  (p. 359).

**Glycidic Acid**,  $C_3H_4O_3$ , an oxide or anhydridic acid, is formed (similar to epichlorhydrin) from  $\beta$ -chlorlactic acid and  $\alpha$ -chlorhydracrylic acid, when treated with alcoholic potash or soda:—



When separated from its salts by sulphuric acid, it is a mobile liquid, miscible with water, alcohol and ether. It volatilizes when heated and possesses a pungent odor. Its *potassium salt*,  $C_3H_3KO_3 + \frac{1}{2}H_2O$ , forms warty, crystalline aggregates. Ferrous sulphate does not color the acid or its salts red (distinction from the isomeric pyroracemic acid). It combines with haloid acids to form  $\beta$ -halogen lactic acids, and on warming with water affords glyceric acid.

Butyl glycidic acid,  $CH_2.CH.CH_2.CO_2H$  and propylene oxycarboxylic acid,



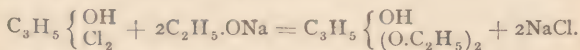
The first is formed when chloroxybutyric acid (from isocrotonic acid and ClOH) is treated with alcoholic potash; it is very unstable when pure; it regenerates the chloroxyacid (melting at  $82^\circ$ ) with HCl. *Propylene Oxycarboxylic Acid* is produced in a similar manner from crotonic acid on treating the latter with ClOH and alcoholic potash. It crystallizes in rhombic prisms and melts at  $84^\circ$  (*Ber.*, 16, 1268).

**Epibromhydrin**,  $C_3H_5OBr$ , from the dibromhydrins, is analogous to epichlorhydrin and boils at  $130-140^\circ$ .

**Epi-iodhydrin**,  $C_3H_5OI$ , results from the treatment of epichlorhydrin with a solution of potassium iodide, and boils at  $160^\circ$ .

### ALCOHOL ETHERS OF GLYCEROL.

Mixed ethers of glycerol with alcohol radicals (p. 105) are obtained by heating the mono- and dichlorhydrins with sodium alcoholates:—



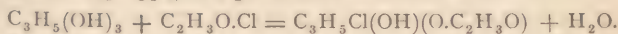
**Monoethylin**,  $C_3H_5 \left\{ \begin{array}{l} (OH)_2 \\ O.C_2H_5 \end{array} \right.$ , is soluble in water, and boils at  $230^\circ$ . **Diethylin**,  $C_3H_5 \left\{ \begin{array}{l} OH \\ (O.C_2H_5)_2 \end{array} \right.$ , is difficultly soluble in water, has an odor resembling that of peppermint, and boils at  $191^\circ$ ; its specific gravity is 0.92. When its sodium compound is treated with ethyl iodide we obtain *Triethylin*,  $C_3H_5(O.C_2H_5)_3$ , insoluble in water, and boiling at  $185^\circ$ .

**Allylin**,  $C_3H_5 \left\{ \begin{array}{l} (OH)_2 \\ O.C_3H_5 \end{array} \right.$ , monoallyl ether, is produced by heating glycerol with oxalic acid, and is present in the residue from the preparation of allyl alcohol (p. 103). It is a thick liquid, boiling at  $225-240^\circ$ .

A compound of the formula,  $C_6H_{10}O_3$ , and designated *glycerin ether*,  $(C_3H_5)_2O_3$ , occurs with allylin, and boils at  $169-172^\circ$  (see *Ber.*, 14, 1946 and 2270).

### ACID ESTERS OF GLYCEROL.

By replacing 1, 2 and 3 hydrogen atoms in glycerol with acid radicals we obtain the so-called *mono*-, *di*-, and *triglycerides*. They are formed when glycerol and fatty acids are heated to  $100-300^\circ$ ; whereas in the action of acid chlorides upon glycerol esters of the chlorhydrins (p. 354) are produced:—



When the acid glycerides are acted upon with alkalies, lime water, or lead oxide, they all revert to glycerol and salts of the fatty acids (soaps) (p. 186). Concentrated sulphuric acid decomposes them into free acids and glycerol sulphuric acid (p. 353).

**Monoformic Ester**,  $C_3H_5 \left\{ \begin{array}{l} (OH)_2 \\ O.CHO \end{array} \right.$ , Monoformin, is produced by heating glycerol with oxalic acid (p. 103). It distils near  $200^\circ$ , and decomposes partly into allyl alcohol,  $CO_2$  and water; it distils without decomposition in vacuo.

**Monacetin**,  $C_3H_5 \left\{ \begin{array}{l} (OH)_2 \\ O.C_2H_3O \end{array} \right.$ , is formed on heating glycerol with glacial acetic acid to  $100^\circ$ . It is a liquid which dissolves readily in water and ether.

**Diacetin**,  $C_3H_5 \left\{ \begin{array}{l} OH \\ (O.C_2H_3O)_2 \end{array} \right.$ , is obtained from glycerol and glacial acetic acid when they are heated to  $200^\circ$ . It boils at  $280^\circ$ .

**Triacetin**,  $C_3H_5(O.C_2H_3O)_3$ , is prepared by prolonged heating of diacetin with an excess of glacial acetic acid to  $250^\circ$ ; it boils at  $268^\circ$ . It is found in slight quantities in the oil of *Euonymus europaeus*.



**Tributyrin**,  $C_3H_5(O.C_4H_7O)_3$ , occurs along with other higher triglycerides in cow's butter.

The glycerides of the higher fatty acids,  $C_nH_{2n}O_2$ , and those of the oleic acid series,  $C_nH_{2n-2}O_2$ , occur in the natural fatty oils, fats, and tallow; they can be obtained artificially by heating glycerol with the acids.

**Monopalmitin**,  $C_3H_5 \left\{ \begin{matrix} (OH)_2 \\ O.C_{16}H_{31}O \end{matrix} \right.$ , melts at  $58^\circ$ . **Dipalmitin**,  $C_3H_5 \left\{ \begin{matrix} OHI \\ (O.C_{16}H_{31}O)_2 \end{matrix} \right.$ , at  $59^\circ$ . **Tripalmitin**,  $C_3H_5(O.C_{16}H_{31}O)_3$ , is found in most fats, especially in palm oil, from which it can be obtained by strong pressing and recrystallization from ether. It separates from olive oil when the latter is strongly cooled. It crystallizes from ether in pearly, glistening laminae, which melt at  $63^\circ$ . By repeated fusion and solidification the melting point falls quite considerably. Like all higher triglycerides it is not very soluble in alcohol.

**Tristearin**,  $C_3H_5(O.C_{18}H_{35}O)_3$ , occurs mainly in solid fats (tallow). It can be obtained by heating glycerol and stearic acid to  $280-300^\circ$ . It crystallizes from ether in shining leaflets, and melts at  $66.5^\circ$ . Its melting point is also lowered by repeated fusion.

**Triolein**,  $C_3H_5(O.C_{18}H_{33}O)_3$ , is found in oils, like olive oil. It solidifies at  $-6^\circ$ . It is oxidized on exposure to the air. Nitrous acid converts it into the isomeric solid elaïdin, which melts at  $36^\circ$  (p. 196).

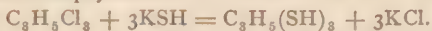
Nearly all the natural fatty oils and fats (tallow) of animal and vegetable origin are mixtures of the triglycerides of the fatty acids. The former are chiefly triolein, the latter (beef tallow, sheep tallow, cocoa butter, etc.), tristearin and tripalmitin. They are insoluble in water, difficultly soluble in alcohol, easily soluble in ether, carbon disulphide, benzene ether, etc. They are lighter than water and swim upon it. They form spots on paper which do not disappear when heated—distinction from the *volatile oils*. They are not volatile, and decompose when strongly heated.

The fatty oils are distinguished as *drying* and *non-drying oils*. The former oxidize readily in the air, are coated with a film and become solid; they comprise the glycerides of the unsaturated acids—linoleic and ricinoleic acids (p. 196). The non-drying oils are glycerides of oleic acid; the production of free acid in them is the cause of their becoming rancid. Among the drying oils are *linseed oil*, *hemp oil*, *walnut oil*, *castor oil*, etc. Non-drying oils are olive oil, rape seed oil (from *Brassica campestris*), also from the oil of *Brassica rapa*, almond oil, train oil and cod oil.

Boiling alkalies saponify all the fats.

#### SULPHUR DERIVATIVES OF GLYCEROL.

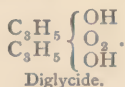
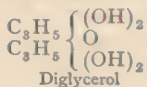
Glycerol mercaptans are formed on heating the chlorhydrins with an alcoholic solution of potassium sulphhydrate:—



The hydrogen atoms in the SH groups can be replaced by heavy metals. Hydrochloric acid precipitates them in the form of thick oils. When oxidized they yield sulpho-acids, which may be prepared from the chlorhydrins by means of alkaline sulphites,

## POLYGLYCEROLS.

They are obtained like the polyglycols (p. 258), viz., by the union of several molecules of glycerol and withdrawal of water. To obtain them, glycerol (diluted  $\frac{1}{3}$  with water), is saturated with HCl and heated to  $130^{\circ}$  for some hours; or glycerol and monochlorhydrin are heated together. They are thick liquids, which can be separated from each other by distillation under diminished pressure. When heated with solid caustic potash they sustain further loss of water and become polyglycides (p. 356):—



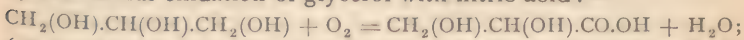
Of the higher trihydric alcohols which have been prepared, we have: **Butyl glycerol**,  $\text{C}_4\text{H}_{10}\text{O}_3 = \text{CH}_3.\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{CH}_2.\text{OH}$ , from the bromide of crotyl alcohol (p. 104), **Amyl glycerol**,  $\text{C}_5\text{H}_9(\text{OH})_3$ , from isoamylene bromide, which has been treated with bromine, and a **Hexyl glycerol**,  $\text{C}_6\text{H}_{11}(\text{OH})_3$ . These are all quite similar to ordinary glycerol.

MONOBASIC ACIDS— $\text{C}_n\text{H}_{2n}\text{O}_4$ .

The acids of this series stand in the same relation to the glycerols, as do the lactic acids to the glycols. They can, too, be regarded as dioxy-fatty acids (p. 350).

The first and lowest dioxyacid (p. 280) has been described as *glyoxylic acid*, (dioxyacetic acid). Both free and in its salts it has one molecule of  $\text{H}_2\text{O}$  firmly combined:  $\text{ClHO.COOH} + \text{H}_2\text{O} = \text{CH}(\text{OH})_2.\text{CO}_2\text{H}$ . However, the two hydroxyl groups do not manifest the usual reactions, but split off water with formation of the aldehyde group.

**Glyceric Acid**,  $\text{C}_3\text{H}_6\text{O}_4$  (dioxypropionic acid), is formed: (1) by the careful oxidation of glycerol with nitric acid:—



(2) by the action of silver oxide upon  $\beta$ -chlorlactic acid,  $\text{CH}_2\text{Cl}.\text{CH}(\text{OH}).\text{CO}_2\text{H}$ , and  $\alpha$ -chlorhydracrylic acid,  $\text{CH}_2(\text{OH}).\text{CHCl}.\text{CO}_2\text{H}$  (p. 356); (3) by heating glycidic acid with water (p. 356).

*Preparation.*—A mixture of 1 volume of glycerol and 1 volume of water is placed in a tall glass cylinder and then 1 part  $\text{HNO}_3$  (sp. gr. 1.5) is introduced by means of a funnel whose end reaches to the bottom of the vessel. Two layers of liquid form and the mixture is permitted to stand for several days at  $20^{\circ}$ , until the layers have completely united. The liquid is then evaporated to syrup consistence, diluted with water, saturated while boiling with calcium carbonate and some lime water added, to precipitate any impurities. When the filtrate is concentrated calcium glycerate separates in warty crusts. It is decomposed with oxalic acid, filtered from the separated oxalate and the filtrate boiled with lead oxide to remove all excess of oxalic acid. Hydrogen sulphide precipitates the lead in this filtrate and the liquid is then concentrated upon a water bath (*Ber.*, 9, 1902, 10, 267, 14, 2071).

Glyceric acid forms a syrup which cannot be crystallized. It is easily soluble in water and alcohol. It is a monobasic acid. Its *calcium salt*,  $(C_3H_5O_4)_2Ca + 2H_2O$ , crystallizes in warty masses, consisting of concentrically grouped needles. It dissolves readily in water but not in alcohol. The *lead salt*,  $(C_3H_5O_4)_2Pb$ , is not very soluble in water. The *ethyl ester*,  $C_3H_5O_4.C_2H_5$ , is formed on heating glyceric acid with absolute alcohol. It is a thick liquid of sp. gr. 1.193 at  $0^\circ$ , and boils at  $230-240^\circ$ . When the acid is heated to  $140^\circ$  it decomposes into water, pyroracemic and pyrotartaric acids. When fused with potash it affords acetic and formic acids and when boiled with it yields oxalic and lactic acids. Phosphorus iodide converts it into  $\beta$ -iodpropionic acid. Heated with hydrochloric acid it yields  $\alpha$ -chlorhydracrylic acid and  $\alpha\beta$ -dichlorpropionic acid.

When glyceric acid is preserved awhile it forms an ester-like modification or anhydride,  $(C_3H_4O_3)_2$  (?). This is difficultly soluble and crystallizes in fine needles, and when boiled with water again reverts to the original acid.

**Amido-glycerol, or Serin**,  $CH_2(OH).CH(NH_2).CO_2H$ ,  $\alpha$ -amidohydracrylic acid, is obtained by boiling serecin with dilute sulphuric acid. It forms hard crystals, soluble in 24 parts water at  $20^\circ$ , but insoluble in alcohol and ether. Being an amido-acid it has a neutral reaction, but combines with both acids and bases. Nitrous acid converts it into glyceric acid.

Isomeric  $\beta$ -amido-lactic acid,  $CH_2(NH_2).CH(OH).CO_2H$ , is obtained from  $\beta$ -chlorlactic acid and glycidic acid by action of ammonia (*Ber.*, 13, 1077). It is more difficultly soluble in water than serin.

The **Hydrate** of trichlorpyroracemic acid,  $CCl_3.CO.CO_2H + H_2O$ , may be considered as an **isotrichlorglyceric acid**,  $CCl_3.C(OH)_2.CO_2H$ . It is formed from trichloracetyl cyanide,  $CCl_3.CO.CN$ , by the action of hydrochloric acid (p. 215). It crystallizes in long needles, melts at  $102^\circ$  and distils undecomposed. It reduces ammoniacal silver solutions and alkaline copper solutions. An interesting method of forming it (along with tricarballic acid) consists in the action of  $KClO_3$  and hydrochloric acid upon gallic acid and phenol.

Of the higher dioxy-acids we may mention **Dioxybutyric Acid**,  $C_4H_8O_4 = C_3H_5(OH)_2.CO_2H$ , obtained from dibrombutyric acid. It is a thick liquid, soluble in water, alcohol and ether. Its isomeride is *Butyl-glyceric Acid*,  $CH_2(OH).CH(OH).CH_2.CO_2H$ , obtained from  $\alpha$ -chlorhydrin with CNK and from butylglycidic acid (p. 356) by addition of water (*Ber.*, 15, 2587).

### DIBASIC ACIDS, $C_nH_{2n-2}O_5$ .

We can regard these as the oxyacids of the dibasic acids,  $C_nH_{2n}(CO_2H)_2$ , from which they are obtained by the introduction of one OH-group for one atom of hydrogen (p. 322).

**Tartronic Acid**,  $C_3H_4O_5 = CH(OH) \begin{smallmatrix} < CO_2H \\ < CO_2H \end{smallmatrix}$ , oxymalonic acid, is produced from chlor- and brom-malonic acid,  $CHCl(CO_2H)_2$ , by

the action of silver oxide or by saponifying their esters with alkalis; from mesoxalic acid,  $\text{CO}(\text{CO}_2\text{H})_2$ , by the action of sodium amalgam; from dibrompyroracemic acid,  $\text{CHBr}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , on warming with baryta water; from glycerol by oxidation with  $\text{MnO}_4\text{K}$ . Also from glyoxylic acid,  $\text{CHO}\cdot\text{CO}_2\text{H}$ , by the action of  $\text{CNH}$  and  $\text{HCl}$ , and from dibromacetic acid,  $\text{CHBr}_2\cdot\text{CO}_2\text{H}$ , when this is first converted into the cyanide,  $\text{CHBr}\begin{smallmatrix} \text{CN} \\ \diagup \\ \text{CO}_2\text{H} \end{smallmatrix}$ .

It is most conveniently prepared from the so-called nitro-tartaric acid, which decomposes on the evaporation of its aqueous solution into  $\text{CO}_2$ ,  $\text{NO}$  and tartronic acid; alcohol accelerates the conversion (*Ber.*, 10, 1789).

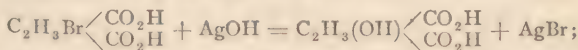
Tartronic acid is easily soluble in water, alcohol and ether, and crystallizes in large prisms. When pure it melts at  $182^\circ$ , decomposing into  $\text{CO}_2$  and glycolide,  $(\text{C}_2\text{H}_2\text{O}_2)_2$  (*Ber.*, 13, 600).

Tartramic Acid,  $\text{CH}(\text{NH}_2)\cdot(\text{CO}_2\text{H})_2$ , was described on p. 322 as amidomalonic acid.

$\text{CH}_2\cdot\text{CO}_2\text{H}$

**Malic Acid**,  $\text{C}_4\text{H}_6\text{O}_5 = \begin{smallmatrix} | \\ \text{CH}(\text{OH})\cdot\text{CO}_2\text{H} \end{smallmatrix}$  **Oxysuccinic Acid**,

(*Acidum malicum*), occurs free or in the form of salts in many plant juices, in unripe apples, in grapes and in mountain-ash berries (from *Sorbus aucuparia*). It is artificially prepared by the action of nitrous acid upon asparagine or aspartic acid (p. 363); by boiling bromsuccinic acid with silver oxide:—



by reduction of tartaric and racemic acids with hydriodic acid (p. 325); by heating fumaric acid with caustic soda to  $100^\circ$  or with water to  $200^\circ$ ; and by saponifying the esters of chlorethenyl-tricarboxylic acid (p. 366).

The best source of malic acid is the juice of unripe mountain-ash berries. This is concentrated, filtered, and while boiling saturated with milk of lime. The pulverulent lime salt which separates is dissolved in hot dilute nitric acid (1 part  $\text{HNO}_3$  in 10 parts water); on cooling acid calcium malate deposits. To obtain the pure acid, the lead salt is prepared and decomposed with  $\text{SH}_2$ .

Malic acid forms deliquescent crystals, which dissolve readily in alcohol, slightly in ether, and melt at  $100^\circ$ . The natural malic acid (from mountain-ash berries) rotates the plane of polarization to the left, that obtained from dextrotartaric acid and aspartic acid turns it to the right. The variety obtained from fumaric and chlorethenyl-tricarboxylic acid is inactive and melts at  $130\text{--}135^\circ$  (*Ann.*, 214, 50). The inactive acid formed in the reduction of racemic acid resembles the product from fumaric acid inasmuch as it can be split into a dextro- and laevo-rotatory malic acid (*Ber.*, 13, 352). In free con-



dition, these modifications exhibit some variations; in their salts, they are chiefly distinguished by their rotatory power. Succinic acid is formed by the reduction of malic acid. This is accomplished by the fermentation of the lime salt with yeast or by heating the acid with hydriodic acid to  $130^{\circ}$  (p. 325). When it is warmed with hydrobromic acid it affords monobrom-succinic acid. Bromine converts malic acid into bromoform and  $\text{CO}_2$ . When the acid alone is heated to  $180^{\circ}$  it decomposes into water, fumaric acid, maleic acid and maleic anhydride (p. 336). When it is heated together with water and some sulphuric acid to  $180^{\circ}$ , it decomposes easily into water and fumaric acid.

The neutral alkali malates do not crystallize well and soon deliquesce; the primary salts, however, do crystallize in good shape. The *primary ammonium salt*,  $\text{C}_4\text{H}_5(\text{NH}_4)\text{O}_5$ , forms large crystals, and when exposed to a temperature of  $160\text{--}200^{\circ}$  becomes *fumarimide*,  $\text{C}_4\text{H}_2\text{O}_2\text{NH}$ .

*Neutral Calcium Malate*,  $\text{C}_4\text{H}_4\text{O}_5\text{Ca} + \text{H}_2\text{O}$ , separates as a crystalline powder on boiling. The acid salt,  $(\text{C}_4\text{H}_5\text{O}_5)_2\text{Ca} + 8\text{H}_2\text{O}$ , forms large crystals which are not very soluble. Sugar of lead precipitates an amorphous *lead salt* from the aqueous solution. On boiling this melts under water.

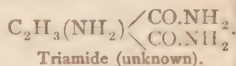
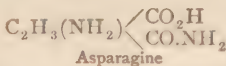
*Sodium Brommalate* (from the acid,  $\text{C}_4\text{H}_5\text{BrO}_5$ ) is formed when the aqueous solution of sodium dibromsuccinate is boiled; milk of lime transforms it into tartaric acid.

The *diethyl ester*,  $\text{C}_4\text{H}_4(\text{C}_2\text{H}_5)_2\text{O}_5$ , suffers partial decomposition when boiled. Acetyl chloride converts it into ethyl aceto-malate,  $\text{C}_2\text{H}_3 \left\{ \begin{array}{l} \text{O.C}_2\text{H}_3\text{O} \\ (\text{CO}_2.\text{C}_2\text{H}_5)_2 \end{array} \right.$ , which boils at  $258^{\circ}$ .

As an isomeride of malic acid may be mentioned:—

*$\alpha$ -Oxyisosuccinic Acid*,  $\text{CH}_3.\text{C}(\text{OH}).(\text{CO}_2\text{H})_2$ , Methyl Tartronic Acid, which is formed from pyroracemic acid,  $\text{CH}_3.\text{CO}.\text{CO}_2\text{H}$ , by means of  $\text{CNH}$ , etc. Isomalic acid, obtained from bromisosuccinic acid by action of silver oxide, is probably identical with the preceding. Both decompose at  $178^{\circ}$  into  $\text{CO}_2$  and  *$\alpha$ -lactic acid*.

### Amides of Malic Acid.



Aspartic acid bears the same relation to malic and succinic acids, as glycollic acid and acetic acid (p. 290); hence it may be designated amidosuccinic acid.

*Malamide*,  $\text{C}_4\text{H}_4\text{O}_3\text{N}_2$ , is formed by the action of ammonia upon dry ethyl malate. It forms large crystals. When heated with water it breaks up into malic acid and ammonia, thus plainly distinguishing itself from isomeric asparagine.

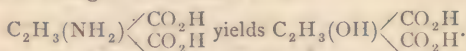
*Ethyl Malamate*,  $\text{C}_2\text{H}_3(\text{OH}) \begin{array}{l} \diagup \text{CO.NH}_2 \\ \diagdown \text{CO}_2.\text{C}_2\text{H}_5 \end{array}$ , is obtained by leading ammonia into the alcoholic solution of malic ester; it forms a crystalline mass.

$\text{CH}(\text{NH}_2).\text{CO}_2\text{H}$

**Aspartic Acid**,  $\text{C}_4\text{H}_7\text{NO}_4 = \begin{array}{c} | \\ \text{CH}_2.\text{CO}_2\text{H} \end{array}$ , amidosuccinic

acid, occurs in the vinasse obtained from the beet root, and is obtained from albuminous bodies in various reactions. It is prepared by boiling asparagine with alkalis and acids. It crystallizes in small rhombic prisms, which are rather readily soluble in hot water. Its alkaline solutions are laevo-rotatory, while its solution in acids, on the other hand, exhibits dextro-rotatory action. Like glycocoll it combines with alkalis and acids yielding salts; with the former it yields acid and neutral salts, *e. g.*,  $\text{C}_4\text{H}_6\text{NO}_4\text{Na} + \text{H}_2\text{O}$  and  $(\text{C}_4\text{H}_6\text{NO}_4)_2\text{Ba} + 3\text{H}_2\text{O}$ .

Nitrous acid changes it to malic acid :—



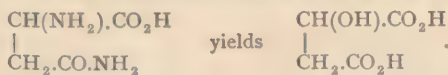
An optically inactive aspartic acid has been obtained by heating fumarimide with water:  $\text{C}_4\text{H}_2\text{O}_2.\text{NH} + 2\text{H}_2\text{O} = \text{C}_4\text{H}_7\text{NO}_4$ . It forms large, monoclinic prisms, and is somewhat more easily soluble in water than the ordinary aspartic acid. Nitrous acid changes it to inactive aspartic acid.

$\text{CH}(\text{NH}_2).\text{CO}_2\text{H}$

**Asparagine**,  $\text{C}_4\text{H}_8\text{N}_2\text{O}_3 = \begin{array}{c} | \\ \text{CH}_2.\text{CO}.\text{NH}_2 \end{array}$ , the monamide of

aspartic acid, is found in many plants, chiefly in their seeds; in asparagus, in beet-root, in peas and beans, etc. It often crystallizes from the pressed juices of these plants after evaporation. It forms shining, four-sided, rhombic prisms, containing 1 molecule of  $\text{H}_2\text{O}$ , and is readily soluble in hot water, but not in alcohol or ether. Its aqueous and alkaline solutions are dextro-rotatory, while the acid solutions are laevo-rotatory. It forms salts with bases and acids (1 equivalent). It is precipitated as a white compound by mercuric nitrate.

It changes to aspartic acid, giving off ammonia, when it is boiled with water; the conversion is more speedy when alkalis or acids are employed. Nitrous acid converts it into malic acid :—



It forms ammonium succinate when it ferments in the presence of albuminoids.

OXY-PYROTARTARIC ACIDS,  $\text{C}_5\text{H}_8\text{O}_5 = \text{C}_3\text{H}_5(\text{OH}) \begin{array}{l} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H} \end{array}$ .

(1) *α*-Oxyglutaric Acid,  $\text{CH}_2 \begin{array}{l} \diagup \text{CH}(\text{OH}).\text{CO}_2\text{H} \\ \diagdown \text{CH}_2.\text{CO}_2\text{H} \end{array}$  (*Ann.*, 208, 66, and *Ber.*, 15,

1157), is obtained by the action of nitrous acid upon glutaminic acid; it occurs in molasses. It crystallizes with difficulty, and melts at  $72^\circ$ . Heated with hydriodic acid it yields glutaric acid (p. 330).

**Glutaminic Acid**,  $\text{CH}_2 \begin{smallmatrix} \diagup \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H} \\ \diagdown \text{CH}_2 \cdot \text{CO}_2\text{H} \end{smallmatrix} = \text{C}_5\text{H}_7(\text{NH}_2)\text{O}_4$ , occurs with aspartic acid in the molasses from beet root, and is formed along with other compounds (p. 289) when albuminoid substances are boiled with dilute sulphuric acid. It consists of brilliant rhombohedra, soluble in hot water but insoluble in alcohol and ether. It melts at  $140^\circ$  and suffers partial decomposition. Like all other amido-acids it affords salts with acids and bases. Mercuric nitrate throws it out of aqueous solution as a white precipitate.

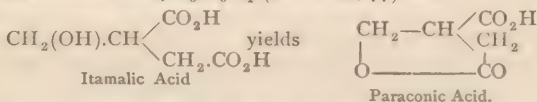
As glutaminic acid is a  $\gamma$ -amido-acid it has power to form an amido-anhydride (a lactam); the resulting (by heating to  $190^\circ$ ) **Pyroglutaminic Acid**,  $\text{C}_5\text{H}_7\text{NO}_3$ , yields pyrrol,  $\text{C}_4\text{H}_5\text{N}$ , (*Ber.* 15, 1322), when heated further:—



(2)  **$\beta$ -Oxyglutaric Acid**,  $\text{CH}(\text{OH}) \begin{smallmatrix} \diagup \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \diagdown \text{CH}_2 \cdot \text{CO}_2\text{H} \end{smallmatrix}$  is obtained from  $\alpha$ -dichlorhydrin (p. 354) by means of potassium cyanide. It forms crystals which dissolve easily in water, alcohol and ether, and melt at  $135^\circ$ .

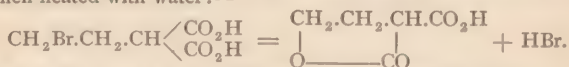
(3) **Oxypyrotartaric Acid**,  $\text{CH}_3 \cdot \text{C}(\text{OH}) \begin{smallmatrix} \diagup \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$ , is produced by the action of  $\text{CNH}$  and hydrochloric acid upon ethyl aceto-acetate, or by oxidizing isovaleric acid with nitric acid (p. 270). It forms a thick syrup, which solidifies in a vacuum and then melts at  $108^\circ$ . Near  $200^\circ$  it decomposes into water and citraconic anhydride.

(4) **Itamalic Acid** is only stable in its salts. When free it decomposes into water and **Paraconic Acid**,  $\text{C}_5\text{H}_6\text{O}_4$  (*Ann.* 218, 77):—



Calcium itamalat is obtained by boiling itachlorpyrotartaric acid (p. 331) with calcium carbonate. Paraconic acid is best prepared by boiling itabrom-pyrotartaric acid with water. It is very deliquescent and melts at  $57-58^\circ$ . When boiled with bases it affords salts of itamalic acid; distilled it yields citraconic anhydride.

(5)  **$\gamma$ -Oxy-ethyl Malonic Acid**,  $\text{CH}_2(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$ . Butyrolactone carboxylic acid is its lactone acid. This is obtained from brom-ethyl malonic acid (melts at  $117^\circ$ —from vinyl malonic acid = trimethylene dicarboxylic acid) when heated with water:—



Heated to  $120^\circ$  it breaks up into  $\text{CO}_2$  and butyrolactone (p. 286).

(6) **Citramalic Acid**,  $\text{C}_3\text{H}_5(\text{OH}) \begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$  is obtained by the action of zinc and hydrochloric acid upon chlorcitramalic acid,  $\text{C}_3\text{H}_5\text{ClO}_3$  (by addition of  $\text{ClOH}$  to citraconic acid). Large crystals, melting at  $119^\circ$  and decomposing at  $130^\circ$  into water and citraconic acid.

(7) **Ethyl Tartronic Acid**,  $\text{C}_2\text{H}_5 \cdot \text{C}(\text{OH}) \begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$  is obtained by chlorinating ethyl malonate,  $\text{C}_2\text{H}_5 \cdot \text{CH}(\text{CO}_2\text{H})_2$ , and subsequently saponifying it with baryta water (p. 323). It melts at  $98^\circ$  and at  $180^\circ$  decomposes into  $\text{CO}_2$  and  $\alpha$ -oxybutyric acid.





UNSATURATED OXYDICARBOXYLIC ACIDS,  $C_nH_{2n-4}O_5$ .

**Oxymaleic Acid**,  $C_4H_4O_5 = C_2H(OH) \begin{smallmatrix} \diagup CO_2H \\ \diagdown CO_2H \end{smallmatrix}$ , is obtained from bromomaleic acid with silver oxide. Soluble needles (*Ber.*, 17, 698).

**Oxyitaconic Acid**,  $C_5H_6O_5$ , is only stable in its salts. Its lactone acid—monobasic **Aconic Acid**,  $C_5H_4O_4$ —results from boiling monobromitaconic acid (from itadibrompyrotartaric acid, p. 331), with water. Soluble rhombic crystals, melting at  $164^\circ$ . It is not capable of combining with bromine (*Ann.*, 216, 91).

**Oxycitraconic Acid**,  $C_5H_6O_5$ , is obtained from chlorcitramalic acid (p. 364) by means of baryta water. It forms readily soluble prisms. It does not unite with bromine or nascent hydrogen, but when heated to  $110^\circ$  with hydriodic acid it is converted into citramalic acid,  $C_5H_8O_5$ .

**Oxyhydromuconic Acid**,  $C_6H_8O_5$ . Its lactone-anhydride, monobasic **Muconic Acid**,  $C_6H_6O_4$ , is obtained by heating dibromadipic acid,  $C_6H_8Br_2O_4$  (from hydromuconic acid, p. 338), with silver oxide. Large, readily soluble crystals, which melt near  $100^\circ$ . It decomposes into  $CO_2$ , and acetic and succinic acids when boiled with baryta water.

TRIBASIC ACIDS,  $C_nH_{2n-4}O_6$ .

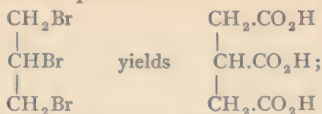
**Formyl Tricarboxylic Acid**, **Methenyl Tricarboxylic Acid**,  $CH(CO_2H)_3 = C_4H_4O_6$ , is decomposed into  $CO_2$  and malonic acid,  $CH_2(CO_2H)_2$ , when it is freed from its esters by alkalis or acids (p. 316). The triethyl ester,  $CH(CO_2C_2H_5)_3$ , is obtained from sodium malonic ester,  $CHNa(CO_2C_2H_5)_2$ , and ethyl chlorocarbonate (p. 315); it is crystalline, melts at  $29^\circ$  and boils at  $253^\circ$ . Sodium alcoholate decomposes it.

**Ethenyl Tricarboxylic Acid**,  $\begin{array}{c} CH_2.CO_2H \\ | \\ CH(CO_2H)_2 \end{array} = C_5H_6O_6$ , is obtained by the saponification of ethyl acetylene tetracarboxylate,  $C_2H_2(CO_2.C_2H_5)_4$  and from esters of cyansuccinic acid,  $C_2H_3(CN)(CO_2R)_2$ . It melts at  $159^\circ$  and decomposes into  $CO_2$  and succinic acid. The *ethyl ester*,  $C_5H_3(C_2H_5)_3O_6$ , is obtained from sodium ethyl malonate and the ester of chloracetic acid. It boils at  $278^\circ$ . Chlorine converts it into **Chlorethenyl Tricarboxylic Ester**,  $C_2H_2Cl(CO_2.C_2H_5)_3$ . This boils at  $290^\circ$ , and when heated with hydrochloric acid yields  $CO_2$ ,  $HCl$ , alcohol and fumaric acid; when saponified with alkalis,  $CO_2$  and malic acid are the products (*Ann.*, 214, 44).

**Methyl Ethenyl Tricarboxylic Acid**,  $C_6H_8O_6 = \begin{array}{c} CH_3-CH.CO_2H \\ | \\ CH(CO_2H)_2 \end{array}$  **propenyl tricarboxylic acid** (isomeric with tricarballylic acid), is obtained by saponifying its esters. It melts at  $146^\circ$ , and falls to  $CO_2$  and ordinary pyrotartaric acid. The *ethyl ester*,  $C_6H_5O_6(C_2H_5)_3$ , is prepared from ethyl sodium malonate and the ester of  $\alpha$ -bromopropionic acid. It boils at  $270^\circ$ .

By the action of sodium alcoholate upon ethenyl tricarboxylic ester, the hydrogen of the  $CH$  group can be replaced by sodium, and this then substituted (by means of alkyl iodides) by alkyls (*Ann.*, 214, 58; *Berichte*, 16, 333). In this way **propyl**-, **isopropyl**-, and **allyl ethenyl carboxylic acids** have been prepared. These part with  $CO_2$  and form the corresponding dicarboxylic acids: **propyl**-, **isopropyl**- and **allyl-succinic acids** (p. 332 and p. 339).

**Tricarballic Acid**,  $C_6H_5O_6 = C_3H_3(CO_2H)_3$ , is obtained :  
 (1) by heating tribromallyl with potassium cyanide and decomposing the tricyanide with potash :—

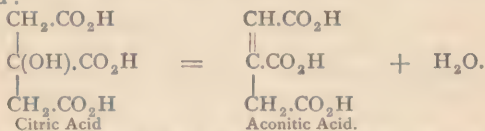


(2) by oxidizing diallyl acetic acid (p. 198); (3) by acting upon ethyl aceto-succinate with sodium and the ester of chloracetic acid, then saponifying the aceto-tricarballic ester (p. 223); (4) by the decomposition of isoallylene-tetracarboxylic acid; (5) by the action of nascent hydrogen upon aconitic acid,  $C_6H_5O_6$ , and by the reduction of citric acid with hydriodic acid; also from so-called dichlorglycide,  $C_3H_4Cl_2$ , and chlorcrotonic ester by the action of potassium cyanide. The acid occurs in unripe beets, and also in the deposit in the vacuum pans used in beet-sugar works. It crystallizes in rhombic prisms, which dissolve easily in water, alcohol and ether, and melt at  $158^\circ$  ( $166^\circ$ ).

The silver salt  $C_6H_5O_6Ag_3$ , is insoluble in water. Calcium tricarballic salt  $(C_6H_5O_6)_2Ca_3 + 4H_2O$ , is a difficultly soluble powder. The triethyl ester,  $C_6H_5O_6(C_2H_5)_3$ , boils near  $300^\circ$ .

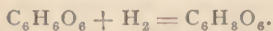
**Aconitic Acid**,  $C_6H_5O_6 = C_3H_3(CO_2H)_3^*$  belongs to the class of unsaturated tricarboxylic acids.

It occurs in different plants, for example, in *Aconitum Napellus*, in *Equisetum fluviatile*, in sugar cane and in beet roots. It is obtained by heating citric acid alone or with concentrated hydrochloric acid :—



Citric acid is rapidly heated in a flask until the formation of white vapors ceases and oily streaks line the neck. The residue is taken up in a little water, evaporated to crystallization, and the crystalline deposit extracted with ether, which will dissolve only aconitic acid. To obtain the latter pure decompose the lead salt with  $H_2S$  (*Ber.* 9, 1751).

Aconitic acid crystallizes in small plates, which dissolve readily in alcohol, ether and water. It melts at  $186-187^\circ$  and decomposes into  $CO_2$  and itaconic acid. Nascent hydrogen converts it into tricarballic acid :—



It gives rise to three series of salts. The tertiary lead salt is insoluble in hot water. The calcium salt  $(C_6H_3O_6)_2Ca_3 + 6H_2O$ , is difficultly soluble. The ethyl ester  $C_6H_3O_6(C_2H_5)_3$ , is a liquid, boiling near  $275^\circ$ .

\* It is isomeric with trimethylene tricarboxylic acid (see this).

Isomeric **Aceconitic Acid**,  $C_6H_6O_6$  (its ethyl ester), is obtained by the action of sodium upon ethyl monobromacetic ester. Here three acetic acid molecules condense. It crystallizes in small needles, and forms salts which are different from those of aconitic acid.

In concluding the di- and tri-valent acids, we may call attention to *Chelidonic* and *Meconic Acids*. Their constitution is as yet undetermined. They are readily converted into pyridine derivatives.

**Chelidonic Acid**,  $C_7H_4O_6$  (?) occurs together with malic acid in *Chelidonium majus*. The juice is boiled, filtered, some nitric acid added and then precipitated with lead nitrate. The lead salt is afterwards decomposed by  $H_2S$ . It crystallizes in silky needles with 1 molecule of  $H_2O$ . These are not very soluble in cold water and alcohol, and melt at  $220^\circ$ . It appears to be a dibasic acid, and it is after the action of alkalis that it yields salts of a tribasic acid. When boiled with alkalis it breaks up into oxalic acid and acetone:—  $C_7H_4O_6 = 2C_2H_2O_4 + C_3H_6O$ . It unites with ammonia, and forms the acid  $C_7H_7NO_6$ , which, on application of heat, splits into  $2CO_2$ ,  $H_2O$  and oxypyridine,  $C_5O_4(OH)N$  (*Ber.*, 16, 1261). Chelidonic acid does not combine with hydroxylamine, hence does not seem to be a ketonic acid.

**Meconic Acid**,  $C_7H_4O_7$ , occurs in opium in union with morphine. The opium extract is saturated with marble, and calcium meconate precipitated by calcium chloride. The salt is afterwards decomposed by hydrochloric acid. It crystallizes with  $3H_2O$  in white laminae, which dissolve readily in hot water and alcohol. At  $100^\circ$  it parts with its water of crystallization. Ferric salts color the acid solutions dark red.

In forming salts the acid generally combines with two equivalents of the bases. The tribasic *silver salt*,  $C_7HAg_3O_7$ , is precipitated by an ammoniacal silver nitrate solution, and has a yellow color.

Meconic acid also unites with ammonia, forming *Comenamic Acid*, which affords *pyridine*,  $C_5H_5N$ , when heated with zinc dust (*Ber.*, 16, 1263; 17, 1507).

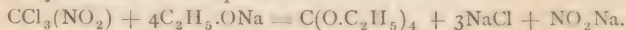
When meconic acid is heated to  $120-200^\circ$  or boiled with water or hydrochloric acid, it decomposes into  $CO_2$  and *Comenic Acid*,  $C_6H_4O_5$ . This is rather insoluble in water, and crystallizes in hard, warty masses. It usually forms salts with one equivalent of base. It unites with hydroxylamine, and hence seems to be a ketonic acid. The *ethyl ester*,  $C_6H_3(C_2H_5)O_5$ , melts at  $135^\circ$ , and forms a nitro-compound which yields *Amidocomenic Acid*,  $C_6H_5NO_5$ , when reduced. Various derivatives of meconic acid can be readily converted into those of picoline or methyl pyridine,  $C_5H_4(CH_3)N$  (*Ber.*, 16, 1373; 17, *Ref.*, 105 and 169).

By the distillation of comenic or meconic acid we obtain *Pyrocomenic Acid*,  $C_5H_4O_3$ , pyromeconic acid. This crystallizes in large, readily soluble plates. It melts at  $117^\circ$ , and sublimes even below  $100^\circ$ . It is monobasic, but possesses a decidedly feeble acid character. It is isomeric with pyromucic acid, and very probably is intimately related to the furfuryl group.

## TETRAVALENT COMPOUNDS.

### TETRAVALENT (TETRAHYDRIC) ALCOHOLS.

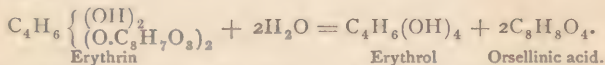
*Ortho-carbonic Ester*,  $C(O.C_2H_5)_4$  (of Basset), may be treated as the ether of the tetrahydric alcohol or normal carbonic acid,  $C(OH)_4$ . It is produced when sodium ethylate acts on chloropicrin:—



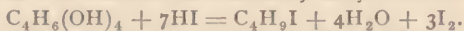
It is a liquid with an ethereal odor, and boils at  $158-159^\circ$ . When heated with ammonia it yields guanidine.

The *propyl ester*,  $C(O.C_3H_7)_4$ , boils at  $224^\circ$ , the *isobutyl ester* at  $250^\circ$ , and it seems the *methyl ester* cannot be prepared (*Ann.*, 205, 254).

**Erythrol, Erythrite**,  $C_4H_{10}O_4 = CH_2(OH).CH(OH).CH(OH).CH_2.OH$ , Erythroglucin or Phycite, occurs free in the alga *Protococcus vulgaris*. It exists as Erythrin (orsellinate of erythrite) in many lichens and some algæ, especially in *Rocella Montagnei*, and is obtained from these by saponification with caustic soda or milk of lime :—



Erythrol forms large quadratic crystals, which dissolve readily in water; in alcohol they are difficultly soluble and in ether insoluble. Like all polyhydric alcohols erythrol possesses a sweet taste. It melts at  $126^{\circ}$  and boils at  $330^{\circ}$  (*Ber.*, **17**, 873). When heated with hydriodic acid it is reduced to secondary butyl iodide:—



Mesotartaric acid is formed when erythrol is oxidized with nitric acid. Erythrol yields esters with acids. The nitric acid ester, the so-called *nitroerythrite*,  $C_4H_6(O.NO_2)_4$ , is obtained by dissolving erythrol in fuming nitric acid; it separates in brilliant plates, melting at  $61^\circ$ . It burns with a bright flame and explodes violently when struck.

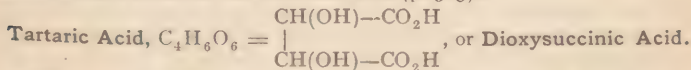
Concentrated hydrochloric acid converts *Erythrol* into the dichlorhydrin,  $C_4H_6(OH)_2Cl_2$  (melting at  $125^\circ$ ). Caustic potash converts this into the dioxide, the so-called *Erythrol ether*,  $CH_2.CH.CH.CH_2$ . This is a pungent-smelling liquid

of sp. gr. 1.113 at 18°; boils at 138° and volatilizes with ether vapors. In its reactions it is perfectly similar to the alkylene oxides (p. 225). It combines gradually with water, forming erythrol, with 2HCl yielding dichlorhydrin, with 2CNH to form the nitrile of dioxyadipic acid, etc. (*Ber.*, 17, 1091).

**Erythritic Acid**,  $C_4H_8O_5 = C_3H_4 \left\{ \begin{matrix} (OH)_3 \\ CO_2H \end{matrix} \right.$ , is produced in the oxidation of an aqueous erythrol solution with platinum sponge, and is a deliquescent crystalline mass. It can form salts with 2 equivalents of the metals.

### DIBASIC ACIDS.

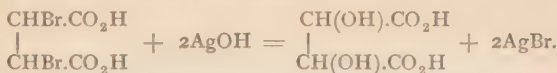
**Dioxymalonic Acid**,  $C_3H_4O_6 = C(OH)_2 \begin{matrix} \diagup CO_2H \\ \diagdown CO_2H \end{matrix}$ , obtained from dibromomalonic acid, is identical with mesoxalic acid (p. 323).



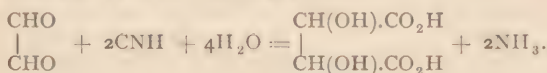
Several modifications of this acid are known; all possess the same structure and can be converted into each other. They are the ordinary or dextro-tartaric acid, lævo-tartaric acid, racemic acid and inactive mesotartaric acid. They are chiefly distinguished by their different optical rotatory power, but all, however, yield the same products of transposition, hence they are viewed as physical isomerides (p. 42).



Dioxysuccinic acid is synthetically prepared by boiling dibromosuccinic acid with moist silver oxide :—



The product in this reaction consists of inactive tartaric acid and racemic acid. Only the latter is formed when CNH and hydrochloric acid (p. 271) act upon glyoxal :—



Racemic acid can yield dextro- and lævo-tartaric acid (p. 372). Heat converts ordinary dextro-tartaric acid and also racemic acid into inactive tartaric acid; conversely, the latter can change to racemic acid by heat (p. 372).

All the tartaric acids, when heated with hydriodic acid, sustain a reduction of the OH- groups and change first to malic and then into succinic acid (p. 324); in this case active tartaric acid yields malic acid, the inactive tartaric, however, inactive malic acid — whereas succinic acid is always inactive (p. 42).

**I. Dextro-rotatory or Ordinary Tartaric Acid** (*Acidum tartaricum*) is widely distributed in the vegetable world, and occurs principally in the juice of the grape, from which it deposits after fermentation, in the form of acid potassium tartrate (argol). It results on oxidizing saccharic and lactic acids with nitric acid.

To prepare tartaric acid crude argol is purified by crystallization and boiled with pulverized chalk and water; this causes it to separate into easily soluble, neutral potassium tartrate and neutral calcium tartrate, which separates as an insoluble powder. Calcium chloride precipitates all the tartaric acid or neutral calcium salt from the filtered solution containing neutral potassium tartrate. The calcium salt is decomposed by dilute  $\text{H}_2\text{SO}_4$ , the gypsum filtered off, and the solution concentrated by evaporation.

Common tartaric acid crystallizes in large monoclinic prisms, which dissolve readily in water and alcohol, but not in ether. Its solution turns the ray of polarized light to the right. It melts at  $135^\circ$ , and in so doing is converted into an amorphous modification, called *metatartaric acid*, which crystallizes again from water as tartaric acid. Heated for some time at  $150^\circ$  water escapes, and we get the anhydrides (p. 274): Ditartronic acid (or tartronic acid),  $\text{C}_8\text{H}_{10}\text{O}_{11}$ , *tartronic acid* and *tartaric anhydride*,  $\text{C}_4\text{H}_4\text{O}_5$ . The latter is a white powder which reverts to tartaric acid when boiled with water. Pyrotartaric and pyrotartaric acids are dry distillation products.

When gradually oxidized tartaric acid becomes oxymalonic acid (p. 360); stronger oxidizing agents decompose it into carbon dioxide and formic acid.

*Tartrates*.—The acid forms salts which contain mainly one and two equivalents of metal; there are, however, some with four equivalents of metal; here four hydrogen atoms (two of the  $\text{CO}_2\text{H}$  groups and two of the  $\text{OH}$  groups) are replaced. The polyvalent acids form such salts with less basic metals, like lead and tin.

The *neutral potassium salt*,  $\text{C}_4\text{H}_4\text{K}_2\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$ , is readily soluble in water; from it acids precipitate the salt  $\text{C}_4\text{H}_5\text{KO}_6$ , which is not very soluble in water, and constitutes natural tartar (*Cremor tartari*).

*Potassium-Sodium Tartrate*,  $\text{C}_4\text{H}_4\text{KNaO}_6 + 4\text{H}_2\text{O}$  (*Seignette's salt*), is made by saturating cream of tartar with a sodium solution. It crystallizes in large prisms with hemihedral faces. The *calcium salt*,  $\text{C}_4\text{H}_4\text{CaO}_6 + 4\text{H}_2\text{O}$ , is precipitated from solutions of neutral tartrates, by calcium tartrate, as an insoluble, crystalline powder. It dissolves in acids and alkalies and is reprecipitated on boiling—a reaction serving to distinguish tartaric from other acids.

The *neutral lead salt*,  $\text{C}_4\text{H}_4\text{PbO}_6$ , is a curdy precipitate. On boiling its ammonia solution a basic salt,  $\text{C}_4\text{H}_2\text{Pb}_2\text{O}_6$ , deposits; in this the hydrogen of all four  $\text{OH}$  groups of tartaric acid is replaced by lead.

*Potassio-antimonious Tartrate*,  $\text{C}_4\text{H}_4(\text{SbO})\text{KO}_6 + \frac{1}{2}\text{H}_2\text{O}$ , tartar emetic. In this an atom of hydrogen is replaced by antimonyl ( $\text{SbO}$ ) (*Ber.*, 13, 1787). It is prepared by boiling cream of tartar with antimony oxide and water. It crystallizes in rhombic octahedrons, which slowly lose their water of crystallization on exposure and fall to a powder. It is soluble in 14 parts water at  $10^\circ$ . Its solution possesses an unpleasant metallic taste, and acts as a sudorific and emetic. When the salt is heated to  $200^\circ$ , 1 molecule of  $\text{H}_2\text{O}$  escapes and we get the basic salt,  $\text{C}_4\text{H}_2\text{SbKO}_6$ , corresponding to basic lead tartrate. Consult *Ber.*, 16, 2379.

The *diethyl ester* of tartaric acid,  $\text{C}_2\text{H}_4\text{O}_2(\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$ , is obtained by conducting  $\text{HCl}$  into a warm alcoholic solution of tartaric acid. It is a liquid which is not soluble in water and partially decomposes on distillation. The *acid ester*,  $\text{C}_2\text{H}_4\text{O}_2 \begin{smallmatrix} \text{CO}_2\cdot\text{C}_2\text{H}_5 \\ \text{CO}_2\text{H} \end{smallmatrix}$ , is formed on evaporating an alcoholic tartaric acid solution. It is a crystalline, deliquescent mass.

When acetyl chloride acts upon the preceding compound the hydrogen of the alcoholic hydroxyl groups is replaced and we obtain acetyl and diethyl diacetyl tartaric esters,  $\text{C}_2\text{H}_2(\text{O}\cdot\text{C}_2\text{H}_5\text{O})_2(\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$ ; the first is a liquid; the second melts at  $67^\circ$ , and boils without decomposition at  $290^\circ$ .

The nitro-group,  $\text{NO}_2$ , can effect the same kind of substitution as noted above (p. 257). By dissolving pulverized tartaric acid in concentrated nitric acid and adding sulphuric acid, so-called *Nitro-tartaric Acid*,  $\text{C}_2\text{H}_2(\text{O}\cdot\text{NO}_2)_2 \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$ , results. This is a gummy mass, which on drying becomes white and shining. It is soluble in water. When its solution is heated tartronic acid is produced. It slowly decomposes into tetra-oxysuccinic acid (p. 378).

*Tartramie Acid*,  $\text{C}_2\text{H}_2(\text{OH})_2 \begin{smallmatrix} \text{CO}\cdot\text{NH}_2 \\ \text{CO}_2\text{H} \end{smallmatrix}$ . Its ammonium salt is obtained by acting on tartaric anhydride,  $\text{C}_4\text{H}_4\text{O}_5$ , with ammonia. From a solution of this salt calcium chloride precipitates calcium tartrate. The acid can be obtained in large crystals from the latter.

*Tartramide*,  $\text{C}_2\text{H}_2(\text{OH})_2 \begin{smallmatrix} \text{CO}\cdot\text{NH}_2 \\ \text{CO}\cdot\text{NH}_2 \end{smallmatrix}$ , is produced by the action of ammonia upon diethyl tartrate.

2. *Lævo-Tartaric Acid* is very similar to the dextro-variety, only differing from it in deviating the ray of polarized light to the left. Their salts are very similar, and usually isomorphous, but those of

the laevo-acid exhibit opposite hemihedral faces. On mixing the two acids, we get the optically inactive racemic acid, which in turn may be separated into the two original acids (see below).

3. *Racemic Acid* is sometimes found in conjunction with tartaric acid in the juice of the grape, and is obtained from the mother liquor in crystallizing cream of tartar.

The mother liquor is boiled and saturated with chalk; the calcium salt which separates is decomposed with sulphuric acid and the filtrate evaporated to crystallization. As the crystals of racemic acid effloresce on exposure to the air, they can be readily separated mechanically from ordinary tartaric acid.

Racemic acid appears in the oxidation of mannitol, dulcitol and mucic acid with nitric acid. It is synthetically obtained from glyoxal by means of prussic and hydrochloric acids, and (together with meso-tartaric acid) from dibromsuccinic acid, by the action of silver oxide (p. 370); in addition, by heating desoxalic acid or its ester (p. 376) with water or dilute acids to  $100^{\circ}$ :  $\text{—C}_5\text{H}_6\text{O}_5 = \text{C}_4\text{H}_6\text{O}_6 + \text{CO}_2$ . An interesting method of preparing it is that of oxidizing fumaric acid with  $\text{MnO}_4\text{K}$  (p. 335).

Racemic acid is most readily made by heating ordinary tartaric acid with water ( $\frac{1}{10}$  part) to  $175^{\circ}$ . The product consists of inactive tartaric acid and racemic acid. These can be separated very easily by crystallization.

Racemic acid crystallizes in prisms having a molecule of water. These slowly effloresce in dry air, and at  $100^{\circ}$  lose their water. It is less soluble in water than tartaric acid, and has no effect on polarized light. Its salts closely resemble those of tartaric acid, but do not show hemihedral faces. The acid potassium salt is appreciably more soluble than cream of tartar. The calcium salt is more difficultly soluble, and is even precipitated by the acid from solutions of calcium chloride and gypsum. Acetic acid and ammonium chloride do not dissolve it.

The acid is composed of dextro- and laevo-tartaric acids. It is most readily converted into these through the sodium-ammonium salt,  $\text{C}_4\text{H}_4\text{Na}(\text{NH}_4)\text{O}_6 + 4\text{H}_2\text{O}$ . On saturating acid sodium racemate with ammonia and allowing it to crystallize, large rhombic crystals form. Some of these show right, others left hemihedral faces. Removing the similar forms, we discover that the former possess right-rotatory power and yield common tartaric acid, whereas the latter afford the laevo-acid. The separation is easier if we project crystal fragments into a supersaturated mixture of the acids. In this case only crystals of the forms introduced will separate. By mixing dextro- and laevo-acid, we again obtain racemic acid.

4. *Inactive Tartaric Acid, Mesotartaric Acid*, is obtained when sorbin and erythrol are oxidized with nitric acid, or when dibromsuccinic acid is treated with silver oxide (p. 370) and maleic acid with  $\text{MnO}_4\text{K}$  (p. 335). It is most readily prepared by heating common tartaric acid with water to  $100^{\circ}$  for several

days. The acid potassium salt affords a means of separating it from unaltered acid and the little racemic acid produced at the same time. At  $175^{\circ}$  more racemic acid is obtained. The latter acid, when heated alone or with water to  $170-180^{\circ}$ , may be changed to the inactive acid. Conversely, when the inactive acid is raised to the same temperature with water, it is transformed into racemic acid; a state of equilibrium occurs between the two acids in solution; this can be overcome by removing one of the acids and by repeated heatings (Jungfleisch).

Mesotartaric acid resembles racemic acid very much. It crystallizes in long prisms containing one molecule of water. These effloresce in the dessicator and then melt at  $140^{\circ}$ . The acid is optically inactive and cannot be directly transformed into the active tartaric acids. Its salts also distinguish it from racemic acid (*Ber.*, 17, 1412).

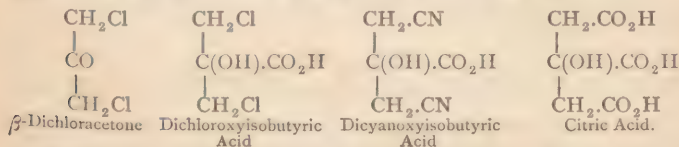
### TRIBASIC ACIDS.

The supposed *Carboxytartronic Acid*,  $C_4H_4O_7 = C(OH)(CO_2H)_3$ , has been proved to be a dibasic acid — *Tetraoxysuccinic Acid*,  $C_2(OH)_4 \cdot (CO_2H)_2 = C_4H_6O_8$  (p. 378).

**Citric Acid**,  $C_6H_8O_7 = C_3H_4(OH)(CO_2H)_3$ , oxytricarballic acid (*Acidum citricum*), occurs free in lemons, in black currants, in bilberry, in beets and in other acid fruits. Commercially it is obtained from lemon juice.

Lemon juice is boiled (to coagulate albuminoid substances), filtered and saturated with calcium carbonate and slacked lime. The calcium salt which separates is decomposed with sulphuric acid and the filtrate concentrated.

The acid can be synthetically prepared from  $\beta$ -dichloroacetone; this is accomplished by first acting on the latter compound with CNH and hydrochloric acid, when we get dichloroxyisobutyric acid (p. 286), which is then treated with KCN and a cyanide obtained, which can be saponified with hydrochloric acid:—



When citric acid is heated it decomposes into water and aconitic acid,  $C_6H_6O_6$  (p. 367), which can receive 2 additional hydrogen atoms and yield tricarballic acid,  $C_3H_5(CO_2H)_3$ ; hence it can be considered as oxytricarballic acid.

Citric acid crystallizes with one molecule of water in large rhombic prisms, which melt at  $100^{\circ}$  and lose water at  $150^{\circ}$ . It dissolves in water of ordinary temperatures, readily in alcohol and with difficulty in ether. The aqueous solution is not precipitated by milk of lime when cold, but on boiling the tertiary calcium salt separates. This is insoluble even in potash (see Tartaric Acid).



When heated to  $170^{\circ}$  citric acid decomposes into water and aconitic acid (p. 367). It breaks up into acetic and oxalic acids when fused with KOH and by oxidation with nitric acid.

Being a tribasic acid it forms three series of salts. Tertiary potassium citrate,  $C_6H_5K_3O_7 + H_2O$ , is made by saturating the acid; it consists of deliquescent needles. The secondary salt,  $C_6H_6K_2O_7$ , is amorphous; the tertiary salt,  $C_6H_7KO_7 + 2H_2O$ , forms large prisms. All three dissolve readily in water. Tertiary calcium citrate,  $(C_6H_5O_7)_2Ca_3 + 4H_2O$  (p. 373), is a crystalline powder. The silver salt,  $C_6H_5Ag_3O_7$ , is a white precipitate which turns black on exposure.

The neutral esters are produced by conducting HCl into hot alcoholic solutions of the acid. The trimethyl ester,  $C_3H_4(OH)(CO_2CH_3)_3$ , is crystalline, melts at  $79^{\circ}$  and distils near  $285^{\circ}$ , decomposing partially at the same time into aconitic ester and water. The triethyl ester,  $C_3H_4(OH)(CO_2C_2H_5)_3$ , boils near  $280^{\circ}$ .

The action of acetyl chloride on the esters replaces the alcoholic hydrogen. The aceto-compound,  $C_3H_4(O.C_2H_3O)(CO_2C_2H_5)_3$ , boils at  $235^{\circ}$ . Nitric acid, too, substitutes the nitro-group for the hydrogen of hydroxyl.

Citramide,  $C_3H_4(OH)(CO.NH_2)_3$ , is formed by the action of  $NH_3$  upon ethyl citrate.

#### TETRABASIC ACIDS.

**Acetylene Tetracarboxylic Ester,**  $\begin{array}{c} CH(CO_2.C_2H_5)_2 \\ | \\ CH(CO_2.C_2H_5)_2 \end{array} = C_6H_2(C_2H_5)_4O_8.$

This is obtained by the action of sodium malonic ester,  $CHNa(CO_2.C_2H_5)_2$ , and chlormalonic ester,  $CHCl(CO_2.C_2H_5)_2$ , or from sodium malonic ester and iodine. It consists of long, shining needles, which melt at  $75^{\circ}$  and boil at  $305^{\circ}$ . It yields a disodium compound with sodium ethylate (*Ber.*, 17, 449). Aqueous potash converts it into ethenyl tricarboxylic acid and  $CO_2$  (p. 366) (*Ann.*, 214, 72).

Sodium and ethyl chloracetate change ethenyl tricarboxylic ester into the ester of **Isoallylene Tetracarboxylic Acid**,  $C(CO_2H)_2 \begin{array}{c} \diagup CH_2.CO_2H \\ \diagdown CH_2.CO_2H \end{array}$ , which boils with slight decomposition at  $295^{\circ}$ . The free acid is obtained by saponifying the ester. It melts at  $151^{\circ}$  and decomposes into  $CO_2$  and tricarballylic acid,  $CH(CO_2H) \begin{array}{c} \diagup CH_2.CO_2H \\ \diagdown CH_2.CO_2H \end{array}$ .

**Dicarbon-Tetracarboxylic Acid,**  $\begin{array}{c} C(CO_2H)_2 \\ || \\ C(CO_2H)_2 \end{array}$ , is an unsaturated compound.

Its tetra-ethyl ester is obtained by letting sodium ethylate act upon chlormalonic ester. Its ester crystallizes in large plates, melting at  $58^{\circ}$ , and boiling near  $325^{\circ}$  (*Ann.*, 214, 77).

#### PENTAVALENT COMPOUNDS.

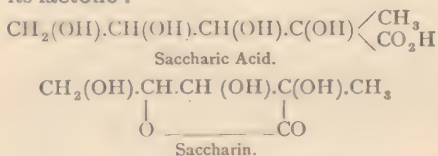
**Quercite**,  $C_6H_{12}O_5 = C_6H_7(OH)_5$ , is a pentahydric unsaturated alcohol. It occurs in acorns, and can be extracted by means of water. Different sugars accompany it, but can be destroyed by fermentation. It crystallizes in hard, monoclinic prisms, which melt at  $235^{\circ}$ , dissolve in 8 parts of water and have a sweet taste. The five hydroxyl groups in it can be substituted by acid radicals.

The penta-acetate,  $C_6H_7(O.C_2H_3O)_5$ , formed on heating quercite with acetic anhydride, is an amorphous deliquescent mass. A very interesting fact in connection with quercite, is that when heated alone or with KOH or hydriodic acid, it affords various derivatives of benzene (Phenol, Quinone, Hydroquinone, Pyrocatechin).

**Pinite**,  $C_6H_{12}O_5$ , seems to have a similar constitution. It exists in the resin of *Pinus lambertina*, and forms wart-like crystals, which melt at  $150^\circ$ .

Quercite and pinite resemble the sugars; they have a sweet taste and are optically active, but do not reduce metallic salts or ferment under the influence of yeast.

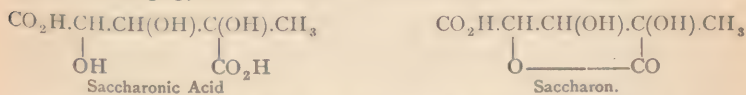
**Saccharic Acid**,  $C_6H_{12}O_6$ , is a monobasic tetrahydric acid. **Saccharin** is its lactone:—



Calcium saccharate is obtained by boiling dextrose and l  vulose (or from invert sugar) with milk of lime. As soon as the acid is liberated from its salts it decomposes into water and saccharin (*Ber.*, 15, 2954). The latter is difficultly soluble in water (in 18 parts), forms large crystals, tastes bitter, melts at  $160^\circ$  and sublimes without decomposition. Hot water changes it in part to saccharic acid (p. 275). It is reduced to symmetrical caprolactone (p. 288) when heated with hydriodic acid and phosphorus (*Ber.*, 16, 182).

Aqueous saccharin possesses right rotatory power; the salts are laevo-rotatory.

**Saccharon**,  $C_6H_8O_6$ , is the lactone of **Saccharonic Acid**,  $C_6H_{10}O_7$ . It is formed when saccharin is oxidized by nitric acid (*Ann.*, 218, 363):—

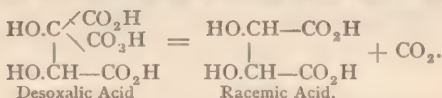


The saccharon crystals have one molecule of water. Its solution deviates polarized light only slightly towards the left. It forms salts  $C_6H_7MeO_6$ , with the carbonates; these change readily to the salts of saccharonic acid,  $C_6H_8Me_2O_7$ . Boiling hydriodic acid and phosphorus reduce it to  $\alpha$ -methyl glutaric acid (p. 322).

When milk sugar is boiled with lime water it yields **Isosaccharin**,  $C_6H_{10}O_5$ . It differs from saccharin and is the lactone of **isosaccharic acid**,  $C_6H_{12}O_6$  (*Ber.*, 16, 2625).

**Aposorbic Acid**,  $C_5H_8O_7 = C_3H_3(OH)_3 \begin{smallmatrix} \diagup CO_2H \\ \diagdown CO_2H \end{smallmatrix}$ , is a dibasic, trihydric acid. It is produced together with tartaric acid on oxidizing sorbin with nitric acid. It crystallizes in small leaflets which melt with decomposition at  $110^\circ$ . It is easily soluble in water and is dibasic.

**Desoxalic Acid**,  $C_5H_6O_8 = C_2H(OH)_2(CO_2H)_3$ , dioxyethenyl tricarboxylic acid, is a tribasic, dihydric acid. Its tri-ethyl ester,  $C_5H_3(C_2H_5)_3O_8$ , results from the action of sodium amalgam upon diethyl oxalate. Large, shining prisms, which melt at  $85^\circ$ . Soluble in 10 parts water and readily in ether. The free acid is obtained by saponifying the ester with baryta water, decomposing the salt with sulphuric acid and slowly evaporating the solution at  $40^\circ$ . The product is a crystalline, deliquescent mass. When its aqueous solution is evaporated or when its ester is heated with water or dilute acids to  $100^\circ$ , the acid yields  $CO_2$  and racemic acid:  $C_5H_6O_8 = C_4H_6O_6 + CO_2$ . Acid radicals can be substituted in the two hydroxyl groups of the desoxalic ester. Heated with hydriodic acid desoxalic acid gives off  $CO_2$  and is reduced to succinic acid. Its structure and transformation into racemic acid are expressed by the following formulas:—

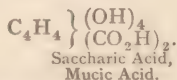
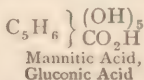
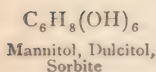


A homologue of desoxalic acid is

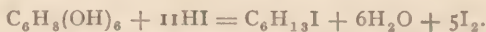
**Oxycitric Acid**,  $C_6H_8O_8 = CH_2(CO_2H).C(OH) \begin{smallmatrix} \diagup CO_2H \\ \diagdown CH(OH).CO_2H \end{smallmatrix}$ , dioxy-tricarballic acid. This accompanies aconitic, tricarballic and citric acids in beet juice, and is produced by boiling chlorcitric acid (from aconitic acid and  $ClOH$ ) with alkalis or water. It crystallizes in needles (*Ber.*, 16, 1078).

**Propargyl Pentacarboxylic Acid**,  $C_8H_8O_{10} = C_3H_3(CO_2H)_5$ , is a pentabasic acid. Its ethyl ester is formed by the action of sodium malonic ester upon chlorethenyl tricarboxylic ester (p. 366).

## HEXAVALENT COMPOUNDS.



Since in all alcohols each carbon atom bears but one hydroxyl group, we would infer that in the hexahydric alcohols, mannitol and dulcitol, the six hydroxyl groups are attached to 6 different carbon atoms. Mannitol, in all probability, is derived from normal hexane,  $C_6H_{14}$ , because when it is reduced with hydriodic acid it yields hexyl iodide:—



Dulcitol yields the same iodide, and is apparently only a physical isomeride.

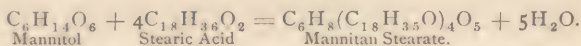
**Mannitol or Mannite**,  $C_6H_{14}O_6$ , occurs rather frequently in plants, chiefly in the sap of the larch, and in the manna-ash (*Fraxinus ornus*), whose dried sap is *manna*. It is produced in the

mucous fermentation of the different varieties of sugar, and may be artificially prepared by the action of sodium amalgam upon grape sugar, but more readily from lævulose ( $C_6H_{12}O_6 + H_2 = C_6H_{14}O_6$ ) (*Ber.*, 16, 3010, 17, 227). Mannitol is also obtained by extracting manna with alcohol and allowing the solution to crystallize.

Mannitol forms delicate needles or rhombic prisms; it dissolves in 5 parts cold water, readily in boiling alcohol, but not in ether. It is inactive, possesses a sweet taste and melts at  $166^\circ$ . When its aqueous solution is permitted to stand in contact with platinum black, **Mannitose**,  $C_6H_{12}O_6$ , is formed; this is probably identical with lævulose (*Ber.*, 17, 227). Nitric acid oxidizes mannitol to saccharic acid,  $C_6H_{10}O_8$ , and oxalic acid, while with  $MnO_4K$  it yields formic, oxalic and a little tartaric acid.

When mannitol is heated to  $200^\circ$  it loses water and forms the anhydrides, **Mannitan**,  $C_6H_{12}O_5$ , and **Mannide**,  $C_6H_{10}O_4$ . The latter is also obtained by distilling mannitol in a vacuum. It melts at  $87^\circ$  and boils at  $274^\circ$  (*Ber.*, 17, Ref. 108).

Mannitol resembles the sugars in combining with bases to yield compounds like  $C_6H_{14}O_6 \cdot CaO$ . When heated with organic acids mannitan esters are usually produced:—



The hexacetate of mannitol,  $C_6H_8(O \cdot C_2H_3O)_6$ , is produced by heating mannitol with acetic anhydride; it is crystalline and melts near  $100^\circ$ .

Mannitol Dichlorhydrin,  $C_6H_8 \left\{ \begin{array}{l} (OH)_4 \\ Cl_2 \end{array} \right.$ , is formed when mannitol is heated with concentrated hydrochloric acid. It consists of laminae. Hydrobromic acid affords the dibromhydrin,  $C_6H_8 \left\{ \begin{array}{l} (OH)_4 \\ Br_2 \end{array} \right.$ .

**Nitro-mannite**,  $C_6H_8(O \cdot NO_2)_6$ , is obtained by dissolving mannitol in a mixture of concentrated nitric and sulphuric acids. From alcohol and ether it crystallizes in bright needles; it melts when carefully heated and deflagrates strongly. When struck it explodes very violently. Alkalies and ammonium sulphide regenerate mannitol.

**Dulcitol**, **Dulcite**,  $C_6H_{14}O_6$ , occurs in various plants and is obtained from dulcitol manna (originating from Madagascar manna). It is made artificially by the action of sodium amalgam upon milk sugar and galactose. It crystallizes in large monoclinic prisms, having a sweet taste. It is more difficultly soluble in water than mannite, and is almost insoluble in boiling alcohol. It melts at  $188^\circ$ . The hexacetate,  $C_6H_8(O \cdot C_2H_3O)_6$ , melts at  $171^\circ$ . Hydriodic acid converts it into the same hexyl iodide that mannitol affords. Nitric acid oxidizes dulcitol to mucic acid.

**Sorbite**,  $C_6H_{14}O_6 + \frac{1}{2}H_2O$ , occurs in mountain-ash berries, forming small crystals which dissolve readily in water. When heated they lose water and melt near  $110^\circ$ .

Mannitol, dulcitol, and sorbite are distinguished from the true



sugars by their inability to undergo fermentation under the influence of yeast; nor are they capable of reducing alkaline copper solutions.

**Isodulcitol**,  $C_6H_{14}O_6$ , is produced from the glucosides quercitrin and xanthoramin on boiling with dilute sulphuric acid. It forms large, lustrous crystals, which melt at  $93^\circ$ . At  $100^\circ$  it loses one molecule of water and forms isodulcitan,  $C_6H_{12}O_5$ , which dissolves in water and affords isodulcitol again. Its rotatory power ( $[\alpha]_D = +8.07$ ) and power to reduce alkaline copper solutions closely ally it with the glucoses. Yeast, however, does not induce it to ferment.

### MONOBASIC ACIDS.

**Mannitic Acid**,  $C_6H_{12}O_7 = C_5H_6 \left\{ \begin{matrix} (OH)_5 \\ CO_2H \end{matrix} \right.$ , is obtained by the action of platinum black upon aqueous mannitol. It is a gummy mass which readily dissolves in water and alcohol. The predominating salts are those in which two equivalents of metal are present.

**Gluconic Acid**,  $C_6H_{12}O_7 = C_5H_6(OH)_5 \cdot CO_2H$ , with normal structure, is formed by the oxidation of dextrose and cane sugar, of dextrine, starch and maltose with chlorine or bromine water and silver oxide (*Ann.*, **220**, 335). It forms a syrup which is almost insoluble in alcohol. Its barium salt crystallizes with three molecules of water, the calcium salt with one. It does not reduce Fehling's solution. Further oxidation converts it into saccharic acid. Normal caprolactone is obtained when the acid is heated with hydriodic acid and phosphorus (*Ber.*, **17**, 1296).

The following acids are closely related to the preceding:—

**Lactonic Acid**,  $C_6H_{10}O_6$ , is produced from milk sugar and galactose by the action of bromine water and silver oxide. It is a deliquescent, crystalline mass, melting at  $100^\circ$  and reducing alkaline copper and silver solutions. It affords glycollic and oxalic acids when heated with silver oxide.

**Glycuronic Acid**,  $C_6H_{10}O_7$ , is formed from campho-glycuronic acid (occurring in the urine of dogs after the ingestion of camphor) and from euxanthic acid on boiling with dilute acids. It changes to its *lactone*,  $C_6H_8O_6$ , on heating its aqueous solution. This new compound crystallizes in thick plates of sweet taste, melts at  $169^\circ$  and decomposes when further heated (*Ber.*, **15**, 1967).

### DIBASIC ACIDS.

**Tetra-oxysuccinic Acid**,  $C_4H_6O_8 = \begin{matrix} C(OH)_2 \cdot CO_2H \\ | \\ C(OH)_2 \cdot CO_2H \end{matrix}$ , Dioxytartaric Acid.

This was formerly regarded as carboxytartronic acid,  $C(OH) \cdot (CO_2H)_3$ . It is obtained when protocatechuic acid, pyrocatechin and guaiacol, in ethereal solution, are acted upon with  $N_2O_3$ , or from nitro-tartaric acid through the action of an alcoholic solution of nitrous acid (*Ann.*, **221**, 246). The addition of sodium carbonate to the aqueous solution separates the *sodium salt*,  $C_4H_4Na_2O_8 + 2H_2O$ , as a difficultly soluble crystalline powder. When heated with water it decomposes into  $CO_2$  and sodium tartronate,  $C_2H_2Na_2O_5$ . On reducing the acid with zinc and hydrochloric acid, it passes into inactive tartaric acid and racemic acid. This deportment is explained by the fact that tetraoxysuccinic acid repre-

sents a diketonic acid,  $\begin{array}{c} \text{CO.CO}_2\text{H} \\ | \\ \text{CO.CO}_2\text{H} \end{array}$ , which, like glyoxylic acid and mesoxalic acid, contains two molecules of water that may be readily split off.

**Saccharic Acid**,  $\text{C}_6\text{H}_{10}\text{O}_8 = \text{C}_4\text{H}_4 \left\{ \begin{array}{l} (\text{OH})_4 \\ (\text{CO}_2\text{H})_2 \end{array} \right.$ , results from the oxidation of mannitol, cane sugar, glucose and many other carbohydrates with nitric acid.

Cane sugar (1 part) is heated with common nitric acid (3 parts) until a stormy reaction sets in, then cooled and heated anew to  $50^\circ$ , until brown vapors cease coming off. The liquid is then diluted with  $\frac{1}{2}$  volume of water, saturated with potassium carbonate, and an excess of acetic acid added. In the course of a few days the primary potassium salt will separate in hard crystals, which may be purified by recrystallization from hot water. The free acid is obtained by decomposing the cadmium salt with hydrogen sulphide.

Saccharic acid forms a deliquescent, gummy mass, readily soluble in alcohol. When prepared from cane sugar its solution is lævo-rotatory and reduces an ammoniacal silver solution. It turns brown at  $100^\circ$  and decomposes. When oxidized with nitric acid dextro-tartaric acid and oxalic acid are formed.

It yields acids and neutral salts. The *primary potassium salt*,  $\text{C}_6\text{H}_9\text{KO}_5$ , and the *ammonium salt*,  $\text{C}_6\text{H}_9(\text{NH}_4)\text{O}_5$ , crystallize well and are difficultly soluble in cold water. The neutral alkali salts are deliquescent; the salts of the heavy metals are insoluble. The *diethyl ester*,  $\text{C}_4\text{H}_4(\text{OH})_4(\text{CO}_2\text{C}_2\text{H}_5)_2$ , is crystalline and is readily soluble in water. With ammonia it forms the *amide*,  $\text{C}_4\text{H}_4(\text{OH})_4(\text{CO.NH}_2)_2$ , a white powder. When acetyl chloride acts on the ester we obtain the *tetra-acetate*,  $\text{C}_4\text{H}_4(\text{O.C}_2\text{H}_3\text{O})_4(\text{CO}_2\text{C}_2\text{H}_5)_2$ , which forms prisms, melting at  $61^\circ$ ; insoluble in water.

See *Ber.*, 17, 246, for an isosaccharic acid.

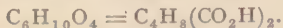
**Mucic Acid**,  $\text{C}_6\text{H}_{10}\text{O}_8 = \text{C}_4\text{H}_4 \left\{ \begin{array}{l} (\text{OH})_4 \\ (\text{CO}_2\text{H})_2 \end{array} \right.$ , is obtained in the oxidation of dulcitol, lactic acid, galactose and nearly all the gum varieties.

1 part of milk sugar and 2 parts nitric acid of sp. gr. 1.4 are heated together, just as in the preparation of saccharic acid from cane sugar (see above). When the solution cools mucic acid separates as a crystalline powder.

It is a white crystalline powder, soluble in 60 parts of boiling water. In cold water and alcohol it is almost insoluble. It melts at  $210^\circ$  with decomposition. When boiled for some time with water it passes into isomeric paramucic acid. Boiling nitric acid decomposes it into racemic acid and oxalic acid. When heated it breaks up, yielding pyromucic acid, which distils over:—



Hydriodic acid reduces it to adipic acid:



The *neutral potassium salt* and *ammonium salt*,  $\text{C}_6\text{H}_8(\text{NH}_4)_2\text{O}_8$ , crystallize

well and are very difficultly soluble in cold water; the *primary* salts dissolve readily. The *silver salt*,  $C_6H_8Ag_2O_8$ , is an insoluble precipitate. When heated the neutral ammonium salt decomposes into  $NH_3$ , water and pyrrol,  $C_4H_5N$ .

The *diethyl ester*,  $C_4H_4(OH)_4(CO_2.C_2H_5)_2$ , is obtained by heating mucic acid and alcohol with sulphuric acid. It is crystalline, is soluble in hot water and melts at  $158^\circ$ . Acetyl chloride converts it into the tetra-acetate, which melts at  $177^\circ$ .

**Butane Hexacarboxylic Acid**,  $C_{10}H_{10}O_{12}$  —  $C_4H_4(CO_2H)_6$ , is a hexabasic acid. Its hexa-ethyl ester is formed by the action of iodine upon the sodium compound of ethenyl tricarboxylic ester (p. 360), and affords large crystals, which melt at  $56^\circ$ .

## CARBOHYDRATES.

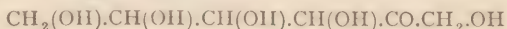
Under this head we understand a group of compounds containing six or a multiple of six atoms of carbon. The hydrogen and oxygen in them are in the same proportion as in water. They are to be viewed as the derivatives of the hexahydric alcohols,  $C_6H_{14}O_6$ . We can arrange them in groups as follows:—

$C_6H_{12}O_6$	$C_{12}H_{22}O_{11}$	$(C_6H_{10}O_5)_n$
Grape Sugar	Cane Sugar,	Dextrine,
or Dextrose,	Milk Sugar,	Gums,
Fruit Sugar	Mycose,	Glycogen,
or Lævulose,	Melitose,	Starch,
Galactose,	Melezitose.	Cellulose.
Arabinose.		

The members of the first group, called glucoses, contain two hydrogen atoms less than the hexahydric alcohols,  $C_6H_8(OH)_6$ , and, indeed, some of them can be converted into the latter by nascent hydrogen. Thus mannitol is produced from dextrose and lævulose, whereas galactose yields dulcitol. As a consequence of this behavior, and from their power of reducing ammoniacal silver and alkaline copper solutions, the glucoses are treated as aldehydes of the hexahydric alcohols according to the formula:—

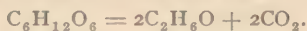


But as the reducing power is not peculiar to the aldehyde group, CHO, only, but also belongs to certain other atomic groupings (p. 150), and as the reaction characteristic of all aldehydes, viz: the reddening of rosaniline solutions by  $SO_2$ , does not occur with the glucoses—it appears possible that the latter are to be regarded as ketone alcohols (p. 213):—

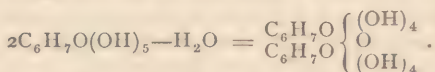


(*Ber.*, 13, 2344, and 14, 2529). An argument favoring this view is the fact that when heated with caustic alkali the glucoses yield acetol,  $CH_3.CO.CH_2.OH$  (p. 213), (*Ber.*, 16, 840). The glucoses may, perhaps, contain an oxygen atom linked as in the lactones (*Ber.*, 16, 923).

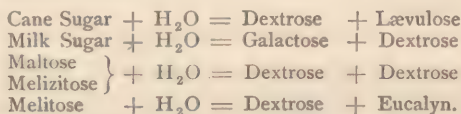
Their fermentation, induced by ferments, is characteristic of the glucoses; they then afford alcohol and  $\text{CO}_2$ :—



The second group,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , comprises the true sugars. They are the anhydrides of the glucoses, formed by the union of two molecules of the latter with elimination of  $\text{H}_2\text{O}$ . They bear the same relation to the glucoses that diethylene glycol and diglycerol do to glycol and glycerol; hence they are termed *disaccharates*:



A confirmation of this view is their absorption of a molecule of water and the production of two molecules of glucoses, when heated with dilute acids. Thus:—



The members of the third group, possessing the empirical constitution,  $\text{C}_6\text{H}_{10}\text{O}_5$ , have probably a higher molecular weight, because when boiled with dilute acids they generally afford several carbohydrates. Thus, starch yields maltose and dextrin, to which the double formula,  $\text{C}_{12}\text{H}_{20}\text{O}_{10}$ , at least, must be ascribed. They can, therefore, be called *polysaccharates*.

The carbohydrates are very often found in plants, some, too, in the animal organism. The cell membranes of all plants consist of cellulose, holding deposits of starch, gums and various sugars. The glucoses are mainly present in unripe fruits.

Direct synthetic methods for the preparation of the carbohydrates are not well known. At various times, however, sweet, sugar-like substances have been obtained, *e. g.*, the so-called methylenitan (*Ber.*, 16, 919), resulting from the action of strong bases upon oxymethylene.

Almost all carbohydrate solutions deviate the plane of polarization to the right; a few to the left. Their specific rotatory power (p. 41) is chiefly governed by temperature and the concentration of their solutions. A phenomenon often shown by the latter, after some standing, is that of a new rotatory power (birotation and semi-rotation, see Racemic Acid). Brief heating of their solutions will usually bring about a recurrence of constant rotation. The determination of the rotatory power of a solution of some definite sugar by means of the saccharimeter is frequently applied in estimating its percentage content—*optical sugar test*.

All the carbohydrates decompose into glucoses when boiled with



dilute acids (p. 381). They sustain an analogous decomposition by the action of various unorganized ferments (albuminoid compounds of unknown constitution), like diastase, which appears in the sprouting of wheat and other grains, or synaptase or emulsin, contained in sweet and bitter almonds. Similar action is exhibited by the soluble ferment of yeast, also saliva, gastric juice and other animal secretions. Thus cane sugar passes into dextrose and levulose, starch into dextrine and maltose, under the influence of yeast.

Fermentation can easily induce a more extended decomposition of many carbohydrates; this is almost always occasioned by the presence of living microscopic organisms, whose germs exist in the air. Therefore the decomposition (fermentation) must be considered the product of the life processes of these organisms, for preservation of which definite conditions are requisite, definite temperature and dilution of solution, presence of albuminoid bodies, mineral salts, air, and the like.

The following varieties of fermentation are known:—

*Alcoholic Fermentation.* This is induced by yeast, which is composed of microscopic (0.01 mm.) cells of *Sacharomyces cerevisie* and *vini*, which multiply during fermentation by budding. Alcoholic fermentation occurs at temperatures varying from 3–35° and is most rapid from 20–30°. Oxygen is requisite at the commencement, but it afterwards proceeds without air access. The glucoses mainly decompose, during fermentation, into alcohol and carbon dioxide:  $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$ . Glycerol (as much as 2.5 per cent.), succinic acid (0.6 per cent.), and fusel oils are formed simultaneously. The glucoses ferment directly; dextrose somewhat more rapidly than levulose. The disaccharates,  $C_{12}H_{22}O_{11}$ , are first decomposed by the soluble ferment of the yeast into glucoses; hence their fermentation proceeds very slowly and demands more yeast.

Other budding fungi, like *Mucor mucedo*, cause alcoholic fermentation. The fermentation phenomena occasioned by *schizomycetes* are exceedingly interesting. It is evident that the production of fusel oils in ordinary yeast fermentation (butyl and amyl alcohol) is due to these.

Alcoholic fermentation can occur unaccompanied by organisms in unimpaired, ripe fruits (grapes, cherries), providing the latter are exposed in an atmosphere of carbon dioxide.

In the *lactic acid* fermentation, the glucoses, milk sugar and gums decompose directly into lactic acid:—



The active agents are little, wand-like organisms (bacteria). Decaying albuminous matter (decaying cheese) is requisite for their development, and it only proceeds in liquids which are not too acid (p. 281). The temperature most favorable varies from 30–50°. By prolonged fermentation the lactates suffer *butyric fermentation*; this is owing to the appearance of other and different organisms (p. 181):  $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$ .

In *mucous fermentation* chain-like cells (of 0.001 mm. diameter) appear. These convert grape sugar, with evolution of  $CO_2$ , into a mucous, gummy substance; mannitol and lactic acid are formed at the same time.

When the glucoses are heated with dilute alkalies they become brown and pass into humus-like bodies. The di- and poly-

saccharates are more stable. When fused with caustic potash or soda all yield oxalic acid. Aided by heat they separate cuprous oxide from alkaline cupric solutions (accomplished through tartaric acid). Indeed, one molecule of glucose reduces almost five atoms of copper as  $\text{Cu}_2\text{O}$ . On this behavior is based the volumetric method of estimating sugar by Fehling's solution. The di- and poly-saccharates do not reduce the latter, even if boiled; maltose only has a reducing action when heated, and milk sugar on boiling.

Hence, in estimating by this method it is necessary to convert the non-reducing sugars into glucoses (inverted sugar) by boiling the former with dilute acids. The glucoses and also maltose and milk sugar reduce solutions of the noble metals in the same manner.

To prepare Fehling's solution, dissolve 36.64 grams of crystallized copper sulphate in water, then add 200 grams Seignette's salt and 600 c.cm of  $\text{NaOH}$  (sp. gr. 1.1200) and dilute the solution to 1 litre. 0.05 gram glucose is required to completely reduce 10 c.c. of this liquid. The end reaction is rather difficult to recognize, hence it is frequently recommended to estimate the separated cuprous oxide gravimetrically (*Ber.*, 13, 826).

The glucoses added to a solution of cupric acetate, containing a little acetic acid (13.3 grams copper acetate and 2 grams glacial acetic acid in 200 c.c. water—Barfoed's Reagent) reduce the salt to  $\text{Cu}_2\text{O}$  at ordinary temperatures; in this case maltose only acts when heated.

Many carbohydrates are capable of combining with bases like  $\text{CaO}$ ,  $\text{BaO}$ , and  $\text{PbO}$ , forming *saccharates*, which correspond to the alcoholates. They afford crystalline compounds with  $\text{NaCl}$  and some other salts.

The hydrogen of the hydroxyls can also be replaced by acid radicals. Nitric-sulphuric acid converts them into nitric esters (nitro-compounds). The esters of acetic acid are best obtained by heating with acetic anhydride, especially in the presence of dehydrating sodium acetate. In this way most all hydroxyls can be substituted.

Usually, elementary analysis affords us no positive conclusion as to the number of acetyl groups which have entered, and we are forced to determine these by saponification with standardized alkali solutions; it is better in many instances to employ magnesia (*Ber.*, 12, 1531), or, decompose the acetyl compounds by boiling with dilute sulphuric acid and titrate the acetic acid which distils over (*Ann.*, 220, 217).

Chlorsulphonic acid,  $\text{SO}_3\text{HCl}$ , converts the carbohydrates, like the mono- and dihydric alcohols, into alkyl sulphuric acids (*Ber.*, 12, 2016).

The *esters* of sugars with organic acids do occur abundantly in plants and are termed *glucosides*. Thus, the tannins are glucosides of aromatic acids. All glucosides afford their components, when heated with acids or alkalies, or through the action of ferments.

Protracted boiling with dilute hydrochloric or sulphuric acid causes the glucoses to be transformed into levulinic acid ( $\beta$ -aceto-propionic acid (p. 224); this is especially true of the l  vuloses. Chlorine water and silver oxide convert

dextrose, cane sugar, dextrin, starch and maltose into gluconic acid,  $C_6H_{12}O_7$  (p. 378), while with silver oxide alone they yield glycollic acid; whereas milk sugar and lactose afford lactic acid,  $C_6H_{10}O_6$ . When dextrose and levulose are boiled with lime they yield the acid,  $C_6H_{12}O_6$  (p. 375). An alkaline copper solution will oxidize dextrose to tartaric acid,  $CH(OH).(CO_2H)_2$ . Nearly all the carbohydrates are oxidized to saccharic or mucic acid by concentrated nitric acid; milk sugar alone yields both acids simultaneously.

The glucoses all combine with phenyl hydrazine,  $C_6H_5.NH.NH_2$ , forming solid crystalline compounds (resembling aldehydes and ketones). (*Ber.*, 17, 579.)

### 1. The Glucoses, $C_6H_{12}O_6$ .

**Grape Sugar, Dextrose,**  $C_6H_{12}O_6 = C_6H_7O(OH)_5$  (p. 380), occurs (always with levulose) in very many sweet fruits and in honey; also contained in the animal organism, in particularly large quantities in the urine in *Diabetes mellitus*. It is formed by the action of dilute acids upon cane sugar, starch, cellulose and many glucosides (p. 381). Its best source (on a large scale) is starch, which yields dextrose only.

Starch (50 parts) is added to boiling dilute sulphuric acid (100 parts  $H_2O$  and 5 parts  $SO_4H_2$ ), in which it dissolves, forming dextrine, which changes into dextrose after several hours' boiling under pressure (*Ber.*, 13, 1761). The sulphuric acid is next saturated with carbonate of lime, the gypsum removed by filtration and the liquid, after filtration through animal charcoal, concentrated. The resulting commercial grape sugar is an amorphous, compact mass, containing only about 60 per cent. dextrose, along with a dextrine-like substance (gallesine,  $C_{12}H_{24}O_{10}$ ), which is not fermentable (*Ber.*, 17, 1000). Pure dextrose with 1 molecule water can be prepared from this, by crystallization, from alcohol. The so-called hard, crystallized grape sugar (of Anthon) appears to be a mixture of the hydrate and anhydride. Its method of preparation is not known.

Dextrose can be got from honey, a mixture of the former and levulose, by spreading it over porous earthen plates; the dissolved levulose is absorbed and the grape sugar remains as a granular, crystalline mass. Levulose is obtained more readily from it by washing with alcohol.

The best method for preparing pure crystallized grape sugar consists in adding to 80 per cent. alcohol, mixed with  $\frac{1}{15}$  volume fuming hydrochloric acid, finely pulverized cane sugar, as long as the latter dissolves on shaking. Pour off the clear liquid and allow to crystallize (*Zeitschrift analyt. Chem.* 15, 192 and *Jour. prakt. Chem.* 21, 244).

Grape sugar crystallizes from water or dilute alcohol, with one molecule of water, in nodular masses, consisting of microscopic rhombic plates; it softens at  $60^\circ$ , melts at  $86^\circ$  and at  $110^\circ$  loses its water of crystallization. It crystallizes from hot absolute alcohol or from methyl alcohol without water, in prisms which melt at  $146^\circ$ . 100 parts of water at  $15^\circ$  dissolve 81.6 parts  $C_6H_{12}O_6$  and 87.8 parts  $C_6H_{12}O_6 + H_2O$ . Anhydrous grape sugar also crystallizes from an aqueous solution (12–15 per cent.  $H_2O$ ) at  $30$ – $35^\circ$  (*Ber.*, 15, 1105).

Aqueous grape sugar exhibits *birotatory* power, *i. e.*, the freshly prepared solution deviates the polarized ray almost twice as strongly as it does after standing some time. At ordinary temperatures the deviation does not become



constant until the expiration of twenty-four hours, whereas when boiled it does so in the course of a few minutes. Furthermore, the specific rotation of dextrose is appreciably augmented by concentration. The true rotatory power of dextrose,  $C_6H_{12}O_6$ , in aqueous solution (p. 41) at  $+20^\circ$ , is:  $A_D = +58.7$  (Tollens).

Grape sugar is not quite so sweet to the taste as cane sugar, and serves to doctor wines. It dissolves without charring in sulphuric acid; alkalis rapidly turn it brown. It reduces salts of the noble metals (an ammoniacal silver solution with production of a silver mirror); precipitates mercury from an alkaline mercuric cyanide solution, and cuprous oxide (on warming) from alkaline cupric solutions (p. 383). Cupric acetate is reduced to  $Cu_2O$  on warming (distinction from dextrine). Ferric salts, also ferricyanide of potassium, are reduced to lower salts. Nascent hydrogen converts grape sugar into mannite; ethyl, isopropyl and  $\beta$ -hexyl alcohol are formed at the same time.

With baryta and lime grape sugar forms saccharates, like  $C_6H_{12}O_6 \cdot CaO$ , and  $C_6H_{12}O_6 \cdot BaO$ . These are precipitated by alcohol. With  $NaCl$  it yields different compounds, of which  $2C_6H_{12}O_6 \cdot NaCl + H_2O$  sometimes separates in the evaporation of urine.

When heated with acetic anhydride we get the diaceto- and tri-aceto compound,  $C_6H_7O \left\{ \begin{array}{l} (OH)_2 \\ (O.C_2H_3O)_3 \end{array} \right.$ ; the latter is not very soluble in water. Further heating with anhydride and sodium acetate yields octoacet-diglucose,  $C_{12}H_{14} (C_2H_3O)_8 O_{11}$ , melting at  $134^\circ$ .

When dextrose and acetyl chloride are heated so-called *aceto-chlorhydrose*,  $C_6H_7O \left\{ \begin{array}{l} Cl \\ (O.C_2H_3O)_4 \end{array} \right.$ , results. A crystalline mass, which nitric acid changes to  $C_6H_7O \left\{ \begin{array}{l} O.NO_2 \\ (O.C_2H_3O)_4 \end{array} \right.$ .

**Fruit Sugar, Lævulose,  $C_6H_{12}O_6$ ,** is found in almost all sweet fruits, together with an equal amount of dextrose. It is likely that cane sugar first forms in the plants and that a ferment at once breaks it up into dextrose and lævulose. It also occurs in honey (together with dextrose). *Invert sugar*, produced by boiling honey with acids or by the action of ferments, consists of equal parts lævulose and dextrose; the latter crystallizes out in sunlight. Lævulose is artificially prepared by carefully oxidizing mannitol with  $MnO_4K$  or nitric acid (*Ber.* 17, 227).

*Preparation.*—Mix 10 parts invert sugar with 6 parts calcium hydrate and 40 parts of water. On pressing the moist mass, the liquid lime compound of dextrose is removed and the residual solid is the lime compound of lævulose. This is decomposed by oxalic acid, the lime oxalate filtered off, and the solution evaporated.

A much readier method is to heat inuline, with water, when it is completely changed to lævulose.

Lævulose forms a thick syrup which at  $100^\circ$  dries to a gummy, deliquescent mass. When the syrup is repeatedly extracted with



cold absolute alcohol, the lævulose gradually crystallizes out in fine, silky needles, of the formula,  $C_6H_{12}O_6$ , which fuse at  $95^\circ$  and lose water at  $100^\circ$ . It is more readily soluble in water and alcohol than dextrose, and rotates the plane to the left more powerfully than dextrose. Its specific rotatory power increases with rising temperature; the influence of concentration is yet undetermined. At  $14^\circ$   $[\alpha]_D$  equals about  $-140^\circ$ . Consequently invert sugar (dextrose and lævulose) is lævo-rotatory. Lævulose is more slowly fermented by yeast than dextrose; therefore in the fermentation of invert sugar the solution finally contains only lævulose. Glycollic acid is produced when chlorine and silver oxide act upon the aqueous solution (dextrose under like conditions affords gluconic acid, p. 378).

In all other reactions lævulose resembles dextrose perfectly, and reduces an alkaline copper solution in the same proportion as dextrose. Oxidized with nitric acid it affords saccharic acid, inactive tartaric and oxalic acids; nascent hydrogen changes it readily into mannitol (*Ber.*, 17, 227).

**Galactose**,  $C_6H_{12}O_6$ , **Lactose**, forms on boiling milk sugar with dilute acids, and is obtained from such gums as yield much mucic acid when oxidized. It crystallizes in nodules of grouped needles or leaflets, which melt at  $166^\circ$ ; it is much more difficultly soluble in water than dextrose, and is almost insoluble in alcohol. Its solution is dextro-rotatory, exhibiting, too, birotation, like grape sugar. It readily reduces alkaline copper solutions, but does not ferment with yeast (*Ber.*, 13, 2305), and does not combine with sodium chloride. Nitric acid oxidizes it to mucic acid, and sodium amalgam converts it into dulcitol.

**Arabinose**,  $C_6H_{12}O_6$ . Gums that yield little or no mucic acid when oxidized with nitric acid are converted into this variety of sugar by dilute sulphuric acid (*Ber.*, 14, 1271). It crystallizes from alcohol in crusts, is dextro-rotatory, reduces alkaline copper solutions, but is not fermented by yeast. Nitric acid does not convert it into mucic acid.

We must probably also include sorbine, inosite, eucalyn, and dambose among the glucoses.

**Sorbine**,  $C_6H_{12}O_6$ , is found in mountain-ash berries, and consists of large crystals, which possess a very sweet taste. It reduces alkaline copper solutions, but is incapable of fermentation under the influence of yeast. Boiling dilute sulphuric acid does not alter it. It undergoes *lactic* fermentation in the presence of chalk and decaying cheese. Oxidized with nitric acid it yields tartaric, racemic acid and ascorbic acids (p. 376). Chlorine and silver oxide convert it into glycollic acid.

**Inosite**,  $C_6H_{12}O_6 + 2H_2O$ , phaseomannite, occurs in many animal organs, principally in the heart muscles and lung tissue; also in various plants, especially in unripe beans (of *Phaseolus vulgaris*) from which it may be extracted with water and precipitated by alcohol.

It yields large rhombic plates or prisms with  $2H_2O$ , which effloresce in the air and melt at  $210^\circ$ . It is soluble in 16 parts water at  $10^\circ$  and possesses a sweet taste. Dilute acids do not affect it. It is inactive, does not reduce alkaline copper solutions and does not ferment with yeast, but yet undergoes lactic fermentation. The following is a very characteristic reaction. If inosite be evaporated almost to dryness with nitric acid, a few drops of ammoniacal calcium chloride then added and the mixture again evaporated, a beautiful rose-red coloration is produced.

Fuming nitric acid converts it into *Hexnitroxyinosite*,  $C_6H_6(O.NO_2)_6$  (nitro-inosite), a yellow oil, which crystallizes. When rapidly heated or when struck it explodes.

**Eucalyn**,  $C_6H_{12}O_6$ , is obtained by the decomposition of melitose and forms a thick syrup. It has dextro-rotatory power; does not reduce copper solutions and is not capable of fermentation.

**Dambose**,  $C_6H_{12}O_6$ , is obtained from its ethers by heating them with fuming hydriodic acid. It crystallizes in six-sided, thick prisms and melts at  $212^\circ$ . Its *dimethyl ether*,  $C_6H_{10}(CH_3)_2O_6$ , occurs in African caoutchouc. Alcohol will extract it from this. It is crystalline, readily soluble in water, melts at  $190^\circ$  and sublimes near  $200^\circ$ . The monomethyl ether,  $C_6H_{11}(CH_3)O_6$ , from Borneo caoutchouc, melts at  $175^\circ$  and sublimes near  $205^\circ$ .

## 2. *Disaccharates*, $C_{12}H_{22}O_{11}$ .

**Cane Sugar**,  $C_{12}H_{22}O_{11} = \begin{matrix} C_6H_7O \\ C_6H_7O \end{matrix} \left\{ \begin{matrix} (OH)_4 \\ O \\ (OH)_4 \end{matrix} \right.$ , Saccharose, (p 380),

occurs in the juice of many plants, chiefly in sugar cane, in some varieties of maple and in beet-roots (10–15 per cent.), from which it is prepared on a commercial scale. While the glucoses occur mainly in fruits, cane sugar is usually contained in the stalks of plants.

Its commercial manufacture from cane or beet sugar is, from a chemical point of view, very simple. The sap obtained by pressing or diffusion is boiled with milk of lime, to saturate the acids and precipitate the albuminoid substances. The juice is next saturated with  $CO_2$ , filtered through animal charcoal, concentrated in a Roberts' Machine, and further evaporated in *vacuum pans* to a thick syrup, out of which the solid sugar separates on cooling. The raw sugar obtained in this manner is further purified with a pure sugar solution, in the centrifugal machine, etc.,—*refined sugar*.

The syrupy mother liquor from the sugar is called molasses; it contains upwards of 50 per cent. cane sugar which is prevented from crystallizing by the presence of salts and other substances. It is either converted into alcohol or the cane-sugar is extracted from it by the fermenting process. The difficultly soluble saccharates of lime and strontium are obtained from the molasses (p. 388) and these are freed from impurities by washing with water or dilute alcohol. The purified saccharates are afterwards decomposed by carbon dioxide, and the juice which is then obtained, after the above plan, is further worked up.

When its solutions are evaporated slowly cane sugar separates in large monoclinic prisms and dissolves in  $\frac{1}{3}$  part  $H_2O$  of medium temperature; it is difficultly soluble in alcohol. Its sp. gr. equals 1.606. Its aqueous solution is lævo-rotatory; the influence of concentration upon the specific rotation is slight; it, however, diminishes (opposite of grape sugar) with increased concentration. Its real rotatory power,  $A_D$ , at  $20^\circ$  is  $64.1^\circ$  (p. 41). Cane sugar melts at  $160^\circ$  and on cooling solidifies to an amorphous glassy mass; in time this again becomes crystalline and non-transparent. At  $190$ – $200^\circ$  it changes to a brown non-crystallizable mass, called *Caramel*, which finds application in coloring liquors.

Cane sugar decomposes into dextrose and lævulose (invert sugar) when boiled with dilute acids. Mixed with concentrated sulphuric

acid it is converted into a black, humus-like body. Saccharic acid, inactive tartaric acid and oxalic acid are formed when it is treated with boiling nitric acid.

Cane sugar yields saccharates (p. 385) with the bases. An aqueous sugar solution readily dissolves lime. If finely divided, burnt lime ( $\text{CaO}$ ) (1 molecule to 1 molecule sugar) be dissolved in a dilute sugar solution (6-12 per cent.) alcohol will precipitate the *monobasic saccharate*,  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{CaO} + 2\text{H}_2\text{O}$ , which, when deprived of its water at  $100^\circ$ , is a white, amorphous mass, that is quite soluble in cold water. Two molecules of  $\text{CaO}$  afford  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{CaO}$ , which separates, in the cold, in beautiful crystals. If  $\text{CaO}$  be added to its solution at temperatures below  $35^\circ$ , all the sugar will be precipitated as tribasic saccharate,  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{CaO}$ ; this is not readily soluble in water. Upon the above deportment is based C. Steffen's substitution process, by which sugar is separated from molasses (*Ber.*, 16, 2764). Strontium and barium give perfectly similar saccharates (*Ber.*, 16, 984). On boiling the sugar solution with lead oxide we get  $\text{C}_{12}\text{H}_{18}\text{Pb}_2\text{O}_{11}$ .

Cane sugar heated to  $160^\circ$  with an excess of acetic anhydride gives *octacetyl ester*,  $\text{C}_{12}\text{H}_{14}\text{O}_8(\text{O} \cdot \text{C}_2\text{H}_3\text{O})_8$ ; this is a white mass, insoluble in water and acetic acid. The action of concentrated nitric acid and sulphuric acid affords the tetranitrate,  $\text{C}_{12}\text{H}_{18}(\text{NO}_2)_4\text{O}_{11}$ , a white mass; it explodes violently.

**Milk Sugar**,  $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O}$ , **Lactose**, has thus far been found in the animal kingdom only, and occurs in the milk of mammals, in the amniotic liquor of the cow, and in certain pathological secretions.

Milk sugar is prepared from whey. This is evaporated to the point of crystallization and the sugar which separates purified by repeated crystallization.

Milk sugar crystallizes in white, hard, rhombic prisms, containing one molecule of water. It is soluble in 6 parts cold or  $2\frac{1}{2}$  parts hot water, has a faint sweet taste, and is insoluble in alcohol. Its aqueous solution is dextro-rotatory and exhibits *birotation* (p. 381). When the constant rotatory point is obtained by heating, the specific rotatory power will vary considerably with the concentration. Milk sugar loses its water of crystallization at  $140^\circ$ , chars, melts at  $205^\circ$ , and suffers further decomposition. It resembles the glucoses in reducing ammoniacal silver solutions; this it effects even in the cold, but in case of alkaline copper solutions boiling is necessary to reach the desired end. Milk sugar yields galactose and dextrose when it is heated with dilute acids; it ferments with difficulty with yeast, but readily undergoes the *lactic* fermentation. Nitric acid oxidizes it into saccharic acid, mucic acid and additional oxidation products. Bromine water and silver oxide convert it into lactonic acid,  $\text{C}_6\text{H}_{10}\text{O}_6$  (p. 378).

An octacetyl ester is obtained by treating the acid with acetic anhydride. A so-called nitro-lactose,  $\text{C}_{12}\text{H}_{17}(\text{NO}_2)_5\text{O}_{11}$ , crystallizes from alcohol in leaflets. This melts at  $139^\circ$  and explodes at  $155^\circ$ .

**Melitose**,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , occurs in the Australian manna (from varieties of *Eucalyptus*), and in cotton seeds; it crystallizes in fine needles, containing  $3\text{H}_2\text{O}$ .



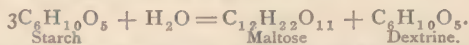
and possesses only a very feeble sweet taste. Two molecules of water escape at  $100^{\circ}$  and the third at  $130^{\circ}$ . Its aqueous solution deviates the plane to the left. It does not reduce copper solutions. It decomposes into dextrose and eucalyn when acted upon by yeast or when heated with dilute sulphuric acid (p. 387).

**Melezitose**,  $C_{12}H_{22}O_{11} + H_2O$ , occurs in the juice of *Pinus Larix*, and resembles cane sugar very much. It is distinguished from the latter by its greater rotatory power and in not being so sweet to the taste.

**Mycose**,  $C_{12}H_{22}O_{11} + 2H_2O$ , Trehalose, occurs in several species of fungi, in ergot of rye, and in the oriental *Trehala*. It is distinguished from cane sugar by its ready solubility in alcohol, greater stability and stronger rotatory power.

**Maltose**,  $C_{12}H_{22}O_{11} + H_2O$ , is a variety of sugar formed together with dextrine by the action of malt diastase (p. 382) upon starch (in the mash of whiskey and beer). It is capable of direct fermentation. It is also an intermediate product in the action of dilute sulphuric acid upon starch, and of ferments (diastase, saliva, pancreas) upon glycogen (p. 390).

In the normal sugaring of pasty starch by diastase, at a temperature of  $50-63^{\circ}$ , nearly  $\frac{2}{3}$  maltose and  $\frac{1}{3}$  dextrine are produced:—



The quantity of maltose produced at more elevated temperatures (above  $63^{\circ}$ ) steadily diminishes up to  $75^{\circ}$  when the action of diastase ceases (*Ber.*, 12, 949). These conditions are important in the manufacture of rum and the brewing of beer. In the first case the mash obtained by the production of sugar at  $60^{\circ}$  is cooled, then the maltose at once ferments and dextrine, in consequence of the after-action of the diastase, is first converted into grape sugar and then fermented; therefore the fermentation of starch is almost a perfect one. In beer-brewing the mash is boiled, to destroy the diastase, so that by the action of ferments only the maltose suffers fermentation; dextrine remains unaltered.

In preparing maltose, starch paste made by boiling with water is converted, at  $60^{\circ}$ , into sugar, by diastase, the solution then boiled, the filtrate concentrated to a syrup and the maltose extracted by strong alcohol (*Ann.*, 220, 209).

Maltose is usually obtained in the form of crystalline crusts composed of hard, white, fine needles, and in properties it closely approaches grape sugar. It is directly fermented by yeast and reduces an alkaline copper solution, but to only about  $\frac{2}{3}$  the amount effected by grape sugar; 100 parts maltose, judging from its reducing power, are equivalent to 61 parts grape sugar, but in the case of Fehling's solution diluted four times, they correspond to about 66.8 parts of the second (*Ann.*, 220, 220). It only acts upon Barfoed's reagent (p. 383) when heat is applied. Its rotatory power is but slightly influenced by the temperature and concentration of the solution,  $[\alpha]_D = +140.6^{\circ}$  (*Ann.*, 220, 200).

Diastase does not exert any further change upon maltose; when boiled with dilute acids it passes completely into grape-sugar. Nitric acid oxidizes it to saccharic acid, while chlorine and silver oxide change it to gluconic acid (p. 378). When heated with sodium acetate and acetic anhydride it affords octoacet-maltose,  $C_{12}H_{14}(C_2H_3O)_8O_{11}$ , which melts at  $150-155^{\circ}$ .



CARBOHYDRATES,  $(C_6H_{10}O_5)_n$ .

**Starch**, Amylum,  $C_6H_{10}O_5$  or  $C_{36}H_{62}O_{31}$ , (p. 381), is found in the cells of many plants, in the form of circular or elongated microscopic granules, having an organized structure. The size of the granules varies, in different plants, from 0.002–0.185 mm. Air dried starch contains 10–20 per cent. water; dried over sulphuric acid it retains some water which is only removed at  $100^\circ$ . Starch granules are insoluble in cold water and alcohol. When heated with water they swell up to  $50^\circ$ , burst, partially dissolve and form *starch paste*, which turns the plane of polarization to the right. The soluble portion is called *granulose*, the insoluble, *starch cellulose*. Alcohol precipitates a white powder—*soluble starch*—from the aqueous solution. The blue coloration produced by iodine is characteristic of starch, both the soluble variety and that contained in the granules. Heat discharges the coloration, but it reappears on cooling.

Boiling dilute acids convert starch into dextrine and dextrose. When heated from  $100$ – $200^\circ$  it changes to dextrine. Malt diastase changes it to dextrine and maltose.

Concentrated sulphuric acid combines with starch, yielding a compound which forms salts with bases. Heated with acetic acid we get the triacetyl derivative,  $C_6H_7O_2(O.C_2H_3O)_3$ , an amorphous mass, which regenerates starch when treated with alkalis. Concentrated nitric acid produces nitrates.

Other starch-like compounds are :—

*Paramylum*,  $C_6H_{10}O_5$ , which occurs in form of white grains in the infusoria *Euglena viridis*. It resembles common starch, but is not colored by iodine, and is soluble in potassium hydrate.

*Lichinine*,  $C_6H_{10}O_5$ , moss starch, occurs in many lichens, and in Iceland moss (*Cetraria islandica*), from which it may be extracted by water. The solution becomes gelatinous, dries to a hard mass, and on treatment with boiling water again forms a jelly. Iodine imparts a dirty blue color to it.

*Inulin* is found in the roots of dahlia, in chicory, and in many Compositæ (like *Inula Helenium*); it is a white powder, which dissolves in boiling water, forming a clear solution. Iodine gives it a yellow color. When boiled with water it is completely changed to lævulose.

*Glycogen*,  $C_6H_{10}O_5$ , animal starch, occurs in the liver of mammals and is a mealy powder, which is precipitated from solution by alcohol; it forms a paste with cold water, and on heating is dissolved in it. Iodine imparts a reddish-brown color to it. Boiling with dilute acids causes it to revert to dextrose, and ferments change it to maltose.

**The Gums**,  $C_6H_{10}O_5$ . These are amorphous, transparent substances widely disseminated in plants; they form sticky masses with water and are precipitated by alcohol. They are odorless and tasteless. Some of them yield clear solutions with water, while others swell up in that menstruum and will not filter through paper. The first are called the *real gums* and the second *vegetable mucilages*. Dilute acids convert them into lactose and arabinose (p. 386).

**Dextrine.** By this name are understood substances, readily soluble in water and precipitated by alcohol; they appear as by-products in the conversion of starch into dextrine, *e. g.*, heating starch alone from  $170-200^{\circ}$ , or by heating it with dilute sulphuric acid. Different modifications arise in this treatment: amylo-dextrine, erythro-dextrine, achro-dextrine; they have received little study. They are gummy, amorphous masses, whose aqueous solutions are dextro-rotatory, hence the name dextrine. They do not reduce Fehling's solution, even on boiling, and are incapable of direct fermentation; in the presence of diastase, however, they can be fermented by yeast (p. 389).

Dextrine is prepared commercially by moistening starch with two per cent. nitric acid, allowing it to dry in the air, and then heating it to  $110^{\circ}$ . It is employed as a substitute for gum.

**Arabin** exudes from many plants, and solidifies to a transparent, glassy, amorphous mass, which dissolves in water to a clear solution. Gum arabic or Senegal gum consists of the potassium and calcium salts of arabic acid. The latter can be obtained pure by adding hydrochloric acid and alcohol to the solution. It is then precipitated as a white, amorphous mass, which becomes glassy at  $100^{\circ}$ , and possesses the composition  $(C_6H_{10}O_5)_2 + H_2O$ . It forms compounds with nearly all the bases; these dissolve readily in water.

Basic lead acetate precipitates gum from its solutions. Its aqueous solution is lævo-rotatory. Nitric acid oxidizes it to mucic, tartaric and oxalic acids.

**Bassorin**, vegetable gum, constitutes the chief ingredient of gum tragacanth, Bassora gum, and of cherry and plum gums (which last also contain arabin). It swells up in water, forming a muciliginous liquid, which cannot be filtered; it dissolves very readily in alkalies.

**Cellulose**,  $C_{12}H_{20}O_{10}$ , forms the principal ingredient of the cell membranes of all plants, and exhibits an organized structure. To obtain it pure, plant fibre, or better, wadding, is treated successively with dilute potash, dilute hydrochloric acid, water, alcohol and ether, to remove all admixtures (incrusting substances). Cellulose remains then as a white, amorphous mass. Fine, so-called Swedish, filter paper consists almost entirely of pure cellulose.

Cellulose is insoluble in the most usual solvents, but dissolves without change in an ammoniacal copper solution. Acids, various salts of the alkalies and sugar precipitate it as a gelatinous mass from such a solution. After washing with alcohol it is a white, amorphous powder. Cellulose swells up in concentrated sulphuric acid and dissolves, yielding a paste from which water precipitates a starch-like compound (amyloid), which is colored blue by iodine. After the acid has acted for some time the cellulose dis-

solves to form dextrine, which passes into sugar, when the solution is diluted with water and then boiled.

So-called parchment paper (vegetable parchment) is prepared by immersing unsized filter paper in sulphuric acid (diluted  $\frac{1}{2}$  with water) and then washing it with water. It is very similar to ordinary parchment, and is largely employed.

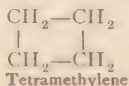
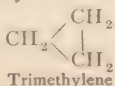
Hexacet-cellulose,  $C_{12}H_{14}O_4(O.C_2H_3O)_6$ , is obtained by heating cellulose (cotton) with acetic anhydride to  $180^\circ$ . It is an amorphous mass, soluble in concentrated acetic acid.

Cold, concentrated nitric acid, or what is better, a mixture of nitric and sulphuric acids, converts cellulose or cotton into esters or so-called *nitro-celluloses*. That these compounds are not nitro-derivatives, but true esters, is manifest, when we consider that upon treatment with alkalis they yield cellulose and nitric acid (p. 353). Alkaline sulphides and ferrous chloride also regenerate cellulose, the nitrogen escaping as ammonia or nitric oxide. The latter only is evolved by iron sulphate in a concentrated hydrochloric acid solution (*Ber.*, 13, 172).

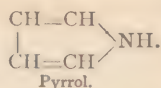
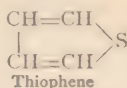
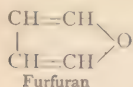
The resulting products exhibit varying properties, depending upon their method of formation. Pure cotton dipped for a period of 3–10 minutes into a mixture of  $HNO_3$  and  $2-3H_2SO_4$ , then carefully washed with water, gives gun cotton (pyroxylin). This is insoluble in alcohol and ether or even in a mixture of the two. It explodes violently if fired in an enclosed space, either by a blow or percussion. It burns violently when ignited in the air, but does not explode. Cotton exposed for some time to the action of a warm mixture of 20 parts pulverized nitre and 30 parts concentrated sulphuric acid becomes *soluble pyroxylin*, which dissolves in ether containing a little alcohol. The solution, termed *collodion*, leaves the pyroxylin, on evaporation, in the form of a thin, transparent film, not soluble in water. It is employed in covering wounds and in photography.

In composition gun cotton is cellulose hexa-nitrate,  $C_{12}H_{14}(O.NO_2)_6O_4$ , whereas the pyroxylin, soluble in ether and alcohol, is essentially a tetra-nitrate,  $C_{12}H_{16}(O.NO_2)_4O_6$ , and a penta-nitrate,  $C_{12}H_{15}(O.NO_2)_5O_5$ , (*Ber.*, 13, 186).

All the compounds considered in the preceding pages, in other words, the so-called *fatty* derivatives, contain *open*, not closed carbon chains, in which terminal and intermediate carbon atoms can be distinguished very readily (p. 25). The numerous derivatives of the benzene class, on the other hand, possess throughout a similar and hence supposed *closed* carbon chain, made up of six carbon atoms. Preceding the very stable benzene nucleus is a class of compounds discovered in recent years, in which we have closed chains. As examples we may mention **trimethylene**,  $C_3H_6$ , and **tetramethylene**,  $C_4H_8$ . **Tetrol**,  $C_4H_4$ , the analogue of benzene, has not yet been obtained:—



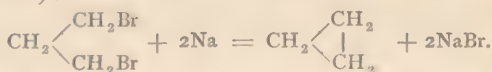
**Furfuran**,  $C_4H_4O$ , **Thiophene**,  $C_4H_4S$ , and **Pyrrol**,  $C_4H_5N$ , are closely allied to tetrol. Their constitution is probably expressed by the following formulas:—



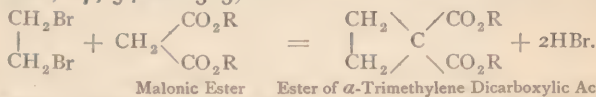
According to this representation, we have here, as in the instance of the lactones (p. 275) and indol derivatives, a chain of four carbon atoms closed by oxygen, nitrogen, or sulphur. From each of these parent substances we can derive a series of compounds by the replacement of hydrogen atoms. In general chemical deportment, furfuran, thiophene and pyrrol exhibit great similarity to the benzene nucleus (p. 398).

### TRIMETHYLENE GROUP.

**Trimethylene**,  $C_3H_6$ , (see above). This is obtained by heating trimethylene bromide (p. 74) with metallic sodium (*Freund*, 1882):—



It is a gas, like its isomeride, propylene (p. 57). It differs from this, in that it unites with difficulty with bromine and hydriodic acid—forming trimethylene bromide and normal propyl iodide. To account for this we assume that the closed ring has been broken. Trimethylene derivatives are produced by the action of alkylene bromides and sodium alcoholates (2 molecules) upon malonic and acetic esters or allied compounds (pp. 217 and 315), (*Perkin, Ber.*, 17, 54 and 323):—



Malonic Ester      Ester of  $\alpha$ -Trimethylene Dicarboxylic Acid.

**Trimethylene-carboxylic Acid**,  $C_3H_5.CO_2H$ , is formed from  $\alpha$ -dicarboxylic acid by heating to  $160^\circ$ . Carbon dioxide is eliminated. It is an oil with faint odor and boils at  $190^\circ$ . It does not unite with bromine, like the isomeric crotonic acids (p. 192). This reagent only acts in a substituting manner, when heat is applied.

**$\alpha$ -Trimethylene-dicarboxylic Acid**,  $C_3H_4(CO_2H)_2$ . Its diethyl ester (see above)  $C_3H_4(CO.C_2H_5)_2$ , is formed from ethylene bromide and malonic ester. It is an oil with an odor resembling that of ethyl malonate, and boils at  $207^\circ$ . The free acid melts at  $140$ – $141^\circ$  and above  $160^\circ$  decomposes into  $CO_2$  and trimethylene carboxylic acid. It does not unite directly with bromine or oxygen, differing thus from the isomeric unsaturated acids,  $C_3H_4O_4$  (p. 337). It, however, combines with  $HBr$ , disrupting the trimethylene ring and forming brom-ethyl malonic acid (p. 364).



**$\beta$ -Trimethylene-dicarboxylic Acid**,  $\text{CH}_2 \begin{array}{c} \diagup \text{CH}.\text{CO}_2\text{H} \\ | \\ \diagdown \text{CH}.\text{CO}_2\text{H} \end{array}$ , is obtained (together

with its anhydride) from trimethylene tricarboxylic acid, by heating the latter to  $190^\circ$ , when  $\text{CO}_2$  splits off. It crystallizes in vitreous prisms and melts at  $137^\circ$ . Its *anhydride*,  $\text{C}_3\text{H}_4(\text{CO})_2\text{O}$ , forms needles, melting at  $57^\circ$  and unites with water at  $140^\circ$ , regenerating the acid.

**Trimethylene-tricarboxylic Acid**,  $\text{CH}_2 \begin{array}{c} \diagup \text{C}(\text{CO}_2\text{H})_2 \\ | \\ \diagdown \text{CH}.\text{CO}_2\text{H} \end{array}$ . The trimethyl ester

is obtained in a manner analogous to that employed in the case of the  $\alpha$ -dicarboxylic ester. It is an agreeably smelling liquid, which boils at  $276^\circ$ . The free acid crystallizes in shining needles and melts at  $184^\circ$ , decomposing into  $\text{CO}_2$  and  $\beta$ -trimethylene-dicarboxylic acid (*Ber.*, 17, 1185.)

**Trimethylene-tetracarboxylic Acid**,  $(\text{CO}_2\text{H})_2\text{C} \begin{array}{c} \diagup \text{CH}.\text{CO}_2\text{H} \\ | \\ \diagdown \text{CH}.\text{CO}_2\text{H} \end{array}$ . Its tetra-

ethyl-ester is obtained from malonic and dibromsuccinic esters. It boils at  $246^\circ$ . The free acid melts at  $95\text{--}100^\circ$ , decomposing into  $\text{CO}_2$  and symmetrical **Trimethylene-tricarboxylic Acid**, which melts at  $147^\circ$  (*Ber.*, 17, 1652).

**$\alpha$ -Aceto-trimethylene Carboxylic Acid**,  $\text{CH}_3.\text{CO}.\text{C}_3\text{H}_4.\text{CO}_2\text{H}$ . Its ester is formed when ethylene bromide and sodium alcoholate act upon aceto-acetic ester:—



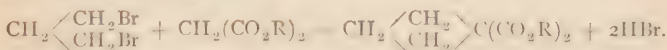
It is a faintly-smelling liquid, boiling about  $195^\circ$ . The free acid is a thick oil, which decomposes at  $200^\circ$  into  $\text{CO}_2$  and **aceto-trimethylene**,  $\text{CH}_3.\text{CO}.\text{C}_3\text{H}_5$ , which boils at  $113^\circ$  (*Ber.*, 17, 1441).

**$\alpha$  Benzoyl-trimethylene Carboxylic Acid**,  $\text{C}_6\text{H}_5.\text{CO}.\text{C}_3\text{H}_4.\text{CO}_2\text{H}$ , is produced, like the preceding, from benzoyl-acetic ester. It forms large prisms, melts at  $149^\circ$ , and decomposes into  $\text{CO}_2$  and **benzoyl-trimethylene**,  $\text{C}_6\text{H}_5.\text{CO}.\text{C}_3\text{H}_5$ . An oil, boiling at  $239^\circ$ .

Boiling alkalies do not decompose benzoyl- and aceto-trimethylene carboxylic acids. Herein they differ from allyl-aceto-acetic (p. 221) and allyl-benzoyl acetic acids (p. 218).

## TETRAMETHYLENE DERIVATIVES.

Tetramethylene derivatives (p. 392) are obtained by acting upon malonic, aceto-, and benzoyl-acetic esters with trimethylene bromide and sodium alcoholate (2 molecules) (Perkin):—



**Tetramethylene-carboxylic Acid**,  $\text{C}_4\text{H}_7.\text{CO}_2\text{H}$ , isomeric with allyl-acetic acid, is formed from the dicarboxylic acid by withdrawal of  $\text{CO}_2$ . It is an oil, which boils at  $194^\circ$ , and has an odor like that of a fatty acid.

**Tetramethylene-dicarboxylic Acid**,  $\text{C}_4\text{H}_6(\text{CO}_2\text{H})_2$ . Its diethyl ester (isomeric with allyl malonic ester, p. 338) is formed from trimethylene bromide and malonic ester (see above). It is an oil with camphor-like odor, and boils at  $224^\circ$  (*Ber.*, 16, 1787). The free acid dissolves easily in ether and benzene,

but not in chloroform and benzene; it crystallizes in shining prisms, and melts at  $155^{\circ}$ , decomposing into the monocarboxylic acid and  $\text{CO}_2$ .

An isomeric **tetramethylene-dicarboxylic acid**,  $\text{CO}_2\text{H} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$ , is obtained from  $\alpha$ -chloropropionic ester by means of sodium ethylate.

**Aceto-tetramethylene Carboxylic Acid**,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CO} \cdot \text{CH}_3 \\ \text{CO}_2 \cdot \text{H} \end{smallmatrix}$  =  $\text{C}_7\text{H}_{10}\text{O}_3$ . The ethyl ester (isomeric with allyl aceto-acetic ester, p. 221) is obtained from aceto-acetic ester and trimethylene bromide. It is a liquid, and boils at  $224^{\circ}$ . The free acid is crystalline, and above  $130^{\circ}$  decomposes into  $\text{CO}_2$  and **Aceto tetramethylene**,  $\text{C}_4\text{H}_7 \cdot \text{CO} \cdot \text{CH}_3$ . A liquid, with camphor-like odor; it boils at  $110^{\circ}$ .

**Benzoyl-tetramethylene Carboxylic Acid**,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{CO}_2 \cdot \text{H} \end{smallmatrix}$ . The ethyl ester (isomeric with allyl-benzoyl-acetic ester), obtained from acetic benzoate, consists of large prisms, melting at  $59^{\circ}$ , and distilling without decomposition. The free acid forms large crystals, which distil at  $143^{\circ}$ , decomposing at the same time into  $\text{CO}_2$  and **benzoyl-tetramethylene**,  $\text{C}_4\text{H}_7 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , an oil, boiling at  $259^{\circ}$ .

None of these tetramethylene derivatives afford bromine addition products, but are substituted by the same when heat is applied.

## FURFURYL GROUP.

**Furfuran**,  $\text{C}_4\text{H}_4\text{O}$  (p. 393), called tetraphenol heretofore, is produced by heating barium pyromucate with soda-lime, and appears, too, to be present in the distillation products of the pine wood. It boils at  $35^{\circ}$ , and is insoluble in water. Hydrochloric acid changes it to an insoluble powder. Another compound, called *sylvan*,  $\text{C}_4\text{H}_3\text{O} \cdot \text{CH}_3$ , occurs in pine-wood oil. It boils at  $63^{\circ}$ , and is, in all probability, methyl furfuran (*Ber.*, 13, 881). Furfuran and also thiophene combine with isatine and phenanthraquinone, yielding dye-stuffs.

**Furfuryl Alcohol**,  $\text{C}_5\text{H}_6\text{O}_2 = \text{C}_4\text{H}_3\text{O} \cdot \text{CH}_2 \cdot \text{OH}$ , is obtained from its aldehyde, furfurol, by the action of sodium amalgam and acetic acid. Ether extracts it as a colorless syrup which on drying becomes resinous. Hydrochloric acid colors it green.

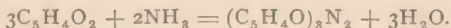
**Furfurol**,  $\text{C}_5\text{H}_4\text{O}_2 = \text{C}_4\text{H}_3\text{O} \cdot \text{CHO}$ , is the aldehyde of furfuryl alcohol. It is obtained in the dry distillation of sugar, or on distilling bran with dilute sulphuric acid or with zinc chloride.

*Preparation.*—Distil 1 part wheat bran with 1 part sulphuric acid, diluted with 3 parts water. The distillate is neutralized with sodium carbonate, then mixed with sodium chloride and again distilled one-half. After the addition of salt the furfurol separates from the distillate in the form of an oil (*Ann.*, 156, 198).

Furfurol is an agreeably-smelling, colorless oil, which browns on exposure to the air. Its specific gravity at  $13^{\circ}$  is 1.163. It boils at  $162^{\circ}$  and dissolves readily in 12 parts  $\text{H}_2\text{O}$  at  $13^{\circ}$  and readily in alcohol. It manifests all the properties of an aldehyde, forming a crystalline compound,  $\text{C}_5\text{H}_4\text{O}_2 \cdot \text{SO}_3\text{NaH}$ , with primary sodium sulphite, is converted into furfuryl alcohol by sodium amalgam, and is

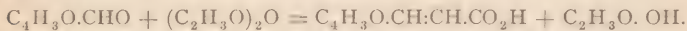
oxidized by silver oxide to pyromucic acid. Alcoholic potash also converts it into furfuryl alcohol and pyromucic acid. It yields *furfuryl aldoxim*,  $C_4H_3O.CH(N.OH)$ , with hydroxylamine; it melts at  $89^\circ$  and boils at about  $205^\circ$ ; it also combines with phenyl hydrazine. Nitric acid oxidizes furfural to oxalic acid.

We get **Furfuramide**,  $(C_5H_4O)_3N_2$ , when furfural stands in contact with aqueous ammonia :—

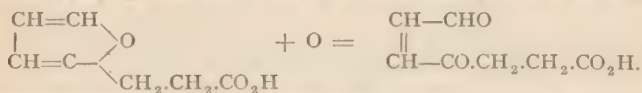


Furfuramide forms white crystals, which melt at  $117^\circ$  and are soluble in alcohol and ether. Boiling water or acids decompose it into furfural and  $NH_3$ . Heated to  $120^\circ$  or boiled with KOH it is converted into isomeric **furfurin**, a base which melts at  $116^\circ$  and forms well crystallized salts with 1 equivalent of acid.

Furfural resembles the aldehydes of the benzene class in uniting with anhydrides of fatty acids to form unsaturated acids (see Cinnamic acid). Thus with acetic anhydride (and sodium acetate) it forms **furfuryl acrylic acid**,  $C_7H_6O_8$  :—



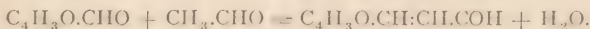
This crystallizes in long needles, which melt at  $135^\circ$ ; it has an odor resembling that of cinnamon and is difficultly soluble in water. Concentrated hydrochloric acid and nitric acid color it green. Sodium amalgam converts it into furfuryl-propionic acid,  $C_4H_3O.CH_2.CH_2.CO_2H$  (melting at  $50^\circ$ ), which yields **furonic aldehyde**,  $C_7H_8O_4$ , when acted upon by bromine water (*Berichte*, 10, 695) :—



Silver oxide oxidizes the latter to **furonic acid**,  $C_7H_6O_5 = C_5H_6O(CO_2H)_2$ . (Fumaric aldehyde and acid are formed in like manner from pyromucic acid, p. 155). Furonic acid crystallizes from hot water in fine needles, which melt at  $180^\circ$ . With nascent hydrogen it unites to form **hydrofuronic acid**,  $C_7H_{10}O_5$ . If this acid be heated with hydriodic acid and phosphorus,  $\alpha$ -pimelic acid,  $C_5H_{10}(CO_2H)_2$ , is produced (p. 332) (*Berichte*, 11, 1358).

**Furfur-butylene**,  $C_4H_3O.CH:C(CH_3)_2$ , is produced by heating furfural with isobutyric anhydride (the latter loses  $CO_2$ ). It is a liquid, boiling at  $153^\circ$ . (*Ber.*, 17, 850).

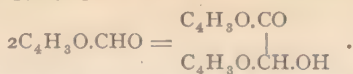
Like the anhydrides of the fatty acids, furfural condenses (like all aldehydes p. 155) with the fatty aldehydes (also with ketones), forming unsaturated aldehydes; the reaction occurs on warming the mixture with dilute sodium hydrate. We thus get **furfur-acrolein**,  $C_7H_6O_2$ , from furfural and aldehyde or paraldehyde :—



Furfur-acrolein forms needles, melting at  $51^\circ$ . Silver oxide converts it into furfur-acrylic acid. Furfur-crotonaldehyde,  $C_4H_3O.CH:C(CH_3).CHO$ , is obtained from furfural and propionic aldehyde.

Furfural, in alcoholic potash solution, when acted upon by potassium cyanide,

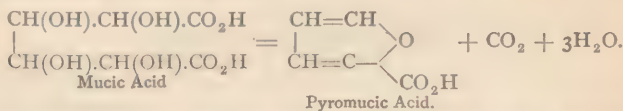
experiences a transformation similar to that of benzaldehyde (see benzoïn). The product is **Furfoïn**,  $C_{10}H_8O_4$  :—



This melts at  $135^\circ$ , and, when in alcoholic solution, is changed by the oxygen of the air to **Furil**,  $C_{10}H_6O_4 = C_4H_3O.CO.CO.C_4H_3O$ . It corresponds to benzil. It crystallizes in golden yellow needles, melting at  $162^\circ$ . CNK and alcohol decompose furil into furfural and the ether of pyromucic acid (*Ber.*, 16, 658). Digested with potash, furil yields isomeric **furilic acid**,  $(C_4H_3O)_2.C(OH).CO_2H$ , corresponding to benzilic acid (see this).

Cyanide of potash converts furfural and benzaldehydes into mixed benzoïns, such as *benzfuroïn* (*Ann.*, 211, 228).

**Pyromucic Acid**,  $C_5H_4O_3 = C_4H_3O.CO_2H$ , is formed by the oxidation of furfural with silver oxide or alcoholic potash, and by the distillation of mucic acid :—

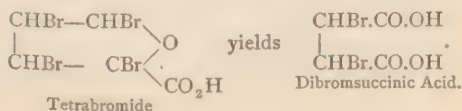


Distil mucic acid from a retort, saturate the distillate with soda, evaporate to dryness, pour sulphuric acid over the residue, and extract the free pyromucic acid with ether. A better procedure is to let alcoholic potash act on furfural; potassium pyromucate separates out, and this can be separated from furfuryl alcohol by means of ether (*Ann.*, 165, 279).

Pyromucic acid is readily soluble in hot water and alcohol, and crystallizes from these in needles or leaflets, melting at  $134^\circ$ . They sublime readily at  $100^\circ$ . Ferric chloride throws out a yellowish-red precipitate from the aqueous solution; in the presence of isopyromucic acid a greenish coloration appears.

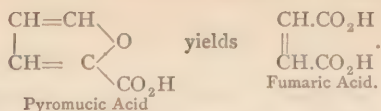
Pyromucic acid is monobasic. The *barium salt*,  $(C_5H_3O_3)_2Ba$ , is readily soluble in water. The *silver salt*,  $C_5H_3O_3Ag$ , crystallizes in leaflets. The *ethyl ester*,  $C_5H_3O_3.C_2H_5$ , is formed by distilling the acid with alcohol and hydrochloric acid. It forms a crystalline mass, melts at  $34^\circ$ , and boils at  $210^\circ$ . The *chloride*,  $C_4H_3O.COCl$ , is produced by distilling the acid with  $PCl_5$ ; it boils at  $170^\circ$ . Ammonia converts this into the *amide*,  $C_4H_3O.CO.NH_2$ , a soluble, crystalline compound, melting at  $143^\circ$ , and passing into *furfuryl nitrile*,  $C_4H_3O.CN$ , upon treatment with  $PCl_3$ . It is a liquid, insoluble in water, and boiling at  $147^\circ$ .

Bromine vapor converts pyromucic acid into a *tetrabromide*,  $C_5H_4Br_4O_3$ , which chromic acid oxidizes to dibromsuccinic acid :—





Bromine water converts pyromucic acid, with elimination of  $\text{CO}_2$ , into fumaric acid :—



Excess of bromine produces mucobromic acid,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_3$ , and chlorine water, too, converts pyromucic acid into mucochloric acid,  $\text{C}_4\text{H}_2\text{Cl}_2\text{O}_3$  (p. 337).

**Isopyromucic Acid**,  $\text{C}_5\text{H}_4\text{O}_3$ , is isomeric with pyromucic acid. It is produced simultaneously with the latter when mucic acid is distilled. It is very readily soluble in cold water. The acid melts at  $82^\circ$  and sublimates below  $100^\circ$ . Pyromeconic acid (p. 368) is isomeric with both these acids.

On heating mucic acid to  $100^\circ$  with hydrobromic acid we obtain :—

**Dehydromucic Acid**,  $\text{C}_6\text{H}_4\text{O}_5 = \text{C}_4\text{H}_2\text{O} \begin{array}{c} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H} \end{array}$ . This is difficultly soluble in water, crystallizes in needles, and when heated decomposes, without melting, into  $\text{CO}_2$  and pyromucic acid.

## THIOPHENE GROUP.

In its entire chemical deportment (like furfuran,  $\text{C}_4\text{H}_4\text{O}$ ) thiophene (p. 393) exhibits very great similarity to benzene,  $\text{C}_6\text{H}_6$ , and affords perfectly analogous derivatives; it may, therefore, be regarded as a benzene in which, without material alteration of properties, one of the three acetylene groups,  $\text{CH}:\text{CH}$ , is replaced by sulphur. The discovery of this remarkable group of compounds was made by V. Meyer in 1883.

**Thiophene**,  $\text{C}_4\text{H}_4\text{S}$ , is present (about 0.6 per cent.) in common commercial benzene, and is artificially prepared by leading ethylene or acetylene through boiling sulphur. Thiophene and all its derivatives acquire an intense dark blue coloration—so-called indophenin reaction (*Ber.*, 16, 1473)—by the action of concentrated sulphuric acid and a small quantity of isatine.

In making thiophene, ordinary coal tar benzene (purified or crude) is shaken for some time with  $\frac{1}{10}$  part concentrated sulphuric acid, until the residual benzene no longer affords the indophenin reaction. In this manner all the thiophene and a portion of the benzene are converted into sulpho-acids. The aqueous solution of the latter is saturated with lead carbonate, and the dry lead salt then distilled with  $\text{NH}_4\text{Cl}$ , when a mixture of thiophene (80 per cent.) and benzene is obtained. This product, after dilution with ligroïne, is subjected again to the same operations (*Ber.*, 16, 1465; 17, 792).

Thiophene is a colorless, mobile oil, of faint odor, and boils at  $84^\circ$ . Its specific gravity equals 1.062 at  $23^\circ$ . It is not attacked by sodium even on boiling; nitric acid oxidizes it energetically. It unites, like benzene, with aldehydes to form condensation products (*Ber.*, 17, 1341).

Thiophene yields substitution products with chlorine and bromine;  $C_4H_3ClS$  boils at  $130^\circ$ ;  $C_4H_2Cl_2S$  at  $170^\circ$ ;  $C_4Cl_4S$  crystallizes in beautiful needles, which melt at  $36^\circ$ , and boil at  $230^\circ$ . Monobromthiophene,  $C_4H_3BrS$ , boils at  $150^\circ$ ;  $C_4H_2Br_2S$  at  $211^\circ$ . Monoiodothiophene,  $C_4H_3IS$ , boils at  $182^\circ$ .

Thiophene (diluted with ligroïne) dissolves in concentrated sulphuric acid, forming a sulpho-acid,  $C_4H_3S.SO_3H$ , which yields well crystallized salts. Separated from the lead salt it is a deliquescent, crystalline mass. Its *chloride*,  $C_4H_3S.SO_2Cl$ , is an oil that will become crystalline; the amide melts at  $141^\circ$ . The reduction of the chloride of the sulpho-acid affords **Thiophene Sulphinic Acid**,  $C_4H_4S.SO_2H$ , crystallizing in needles, and melting at  $67^\circ$ .

When potassium thiophene-sulphonate is distilled with CNK or  $K_4Fe(CN)_6$ , **Thiophennitrile**,  $C_4H_3S.CN$ , is formed. This resembles benzonitrile, and is an oil with an odor like that of bitter almonds; it boils at  $190^\circ$ . On boiling the nitrile with alcoholic potash we obtain—

**Thiophenic Acid**,  $C_4H_3S.CO_2H$ , which shows much similarity to benzoic acid,  $C_6H_5.CO_2H$ . It crystallizes from hot water and sublimes in forms much like those of benzoic acid, melts at  $118^\circ$ , and boils at  $258^\circ$ . Its vapors, like those of benzoic acid, produce coughing. It is readily volatile, with aqueous vapor.

Like benzene, thiophene forms various perfectly analogous condensation products. It unites with methylal, forming **dithiënyl methane**,  $(C_4H_3S)_2CH_2$ , analogous to diphenyl methane,  $(C_6H_5)_2CH_2$ . Benzoyl chloride and  $AlCl_3$  convert it into **dithiënyl phenyl ketone**,  $C_6H_5.CO.C_4H_3S$ , etc., which melts at  $55^\circ$ , and boils at  $300^\circ$ . It is analogous to benzophenone.

When thiophene is conducted through tubes raised to a red heat it forms **Dithiënyl**,  $C_4H_3S.C_4H_3S$ , corresponding to diphenyl. It forms shining leaflets, melting at  $83^\circ$ .

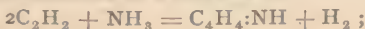
**Thiotolene**,  $C_4H_3S.CH_3$ , or methylthiophene, is a homologue of thiophene. This occurs in the toluene of coal tar, and is extracted in the same manner as thiophene. It is obtained perfectly pure by acting upon its iodide (prepared by heating with iodine and  $HgO$ ) with sodium and alcohol (*Ber.* 17, 787). It is very similar to toluene,  $C_6H_5.CH_3$ ; it is an oil, boiling at  $113^\circ$ , and possesses a specific gravity of 1.0194 at  $18^\circ$ . When thiotolene is added to a glacial acetic acid solution of anthraquinone an intense blue coloration results; by the addition of water a dye substance separates, which is soluble in ether and imparts to it a deep violet coloration (Reaction of Laubenheimer) (*Ber.*, 17, 1338).

The homologous thiophenes can be synthetically prepared by acting upon iodothiophene,  $C_4H_3IS$ , with alkyl iodides and sodium (like the homologous benzenes) (*Ber.*, 17, 1559). The resulting **methyl thiophene**,  $C_4H_3S.CH_3$ , is identical with thiotolene. **Ethyl thiophene**,  $C_4H_3S.C_2H_5$ , boils at  $133^\circ$ ; **propyl thiophene** at  $158^\circ$ ; **butyl thiophene** at  $181^\circ$ .

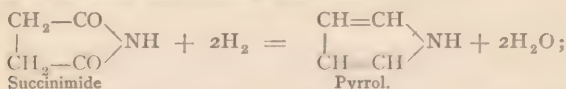
Consult *Ber.* 17, 1563 upon the isomerides of thiophene derivatives.

## PYRROL GROUP.

**Pyrrol**,  $C_4H_5N = C_4H_4:NH$  (p. 393), was first found in coal tar, and is contained in Dippel's oil; it is produced by the union of acetylene with ammonia at a red heat:—



or by the distillation of neutral ammonium mucate or saccharate, and from ammonium pyromucate and carbopyrrolic acid (p. 401). An interesting method for producing it consists in heating succinimide with zinc hydroxide containing zinc dust:—



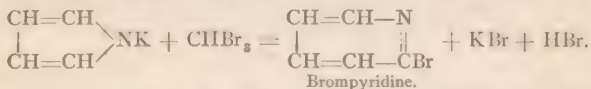
or by heating pyroglutaminic acid (p. 364). Tetrachlorpyrrol,  $\text{C}_4\text{Cl}_4\text{:NH}$ , is produced in a like manner, from dichlormaleic imide (p. 337) by the action of  $\text{PCl}_5$ . Pyrrol is a colorless liquid, with an odor like that of chloroform; it browns on exposure and boils at  $130\text{--}131^\circ$  (corr.); its sp. gr. at  $12.5^\circ$  is 0.9752. It is not very soluble in water, but readily so in alcohol and ether. Its vapors impart a deep red color to a pine shaving moistened with hydrochloric acid. Pyrrol is a weak base, dissolving only slowly in cold dilute acid, and when heated  $\text{NH}_3$  is liberated, and it passes into an amorphous brown powder—pyrrol red,  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}(?)$ .

Pyrrol yields an indigo-blue coloring substance with isatine, and with benzoquinone and with phenanthraquinone violet dyes (*Ber.*, 17, 1034).

Iodine converts pyrrol potassium,  $\text{C}_4\text{H}_4\text{NK}$ , into tetraiodopyrrol,  $\text{C}_4\text{I}_4\text{NH}$ , which crystallizes in yellow-brown prisms and decomposes about  $140^\circ$ . Tetrachlorpyrrol,  $\text{C}_4\text{Cl}_4\text{NH}$ , from perchlorpyrocoll (p. 402), crystallizes in colorless leaflets and melts with decomposition at  $110^\circ$ . (*Ber.*, 16, 2390).

Nascent hydrogen converts pyrrol into **Hydropyrrol**,  $\text{C}_4\text{H}_6\text{NH}$ , **Pyrrolin** (p. 402).

The production of chlor- and brompyridine on heating pyrrol potassium with  $\text{CHCl}_3$  and  $\text{CHBr}_3$ , or with  $\text{CCl}_4$  (*Ber.*, 15, 1179), is rather remarkable:—



Pyrrol is a secondary amine. Heated with acetic anhydride it yields (together with pseudo-acetyl pyrrol, p. 402) *acetyl pyrrol*,  $\text{C}_4\text{H}_4\text{N.C}_2\text{H}_3\text{O}$ . This is an oil which volatilizes with steam, has a characteristic odor, and boils at  $177\text{--}178^\circ$ . An easier method of forming it consists in heating pyrrol potassium with acetyl chloride. Boiling alkalies convert it into pyrrol and acetic acid (*Ber.*, 16, 2352).

Potassium dissolves in pyrrol to form  $\text{C}_4\text{H}_4\text{NK}$ , pyrrol potassium—a white amorphous powder, decomposed by water into pyrrol and  $\text{KOH}$ . Alkyl iodides act on it to produce alkylic pyrrols,  $\text{C}_4\text{H}_4\text{NR}$ . These are also produced, in a manner similar to the formation of pyrrol, by the distillation of the amine salts of the mucic and saccharic acids, and from alkylic succinimides.

**Methyl pyrrol**,  $\text{C}_4\text{H}_4\text{:N.CH}_3$ , boils at  $112\text{--}113^\circ$ ; sp. gr. at  $10^\circ$  is 0.9203. **Ethyl pyrrol**,  $\text{C}_4\text{H}_4\text{:N.C}_2\text{H}_5$ , boils at  $131^\circ$ ; sp. gr. at  $10^\circ$  is 0.9042. **Amyl pyrrol**,  $\text{C}_4\text{H}_4\text{:N.C}_5\text{H}_{11}$ , boils at  $180\text{--}184^\circ$ . **Allyl pyrrol**,  $\text{C}_4\text{H}_4\text{:N.C}_3\text{H}_5$ , be-

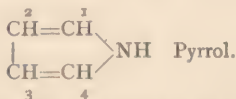
comes a resin by distillation. **Phenyl pyrrol**,  $C_4H_4N.C_6H_5$ , from aniline saccharate and mucate, forms glistening scales with an odor like that of camphor, and melting at  $62^\circ$ .

The alkylized pyrrols are very similar to pyrrol, but are less readily altered by acids. Ethyl pyrrol combines with bromine water, forming the tetrabromide,  $C_4H_4Br_4.N.C_2H_5$ , which crystallizes from alcohol in shining needles, melting at  $90^\circ$ .

The isomerides of the alkyl pyrrols,  $C_4H_4:NR$ , are the *homologous pyrrols*,  $C_4H_3R:NH$ , formed by the introduction of alkyls into the group  $C_4H_4$ . They contain the imide group, and occur in Dippel's oil (*Oleum animale Dippeli*) which is formed in the dry distillation of bones.

Dippel's oil represents a mixture of various substances. The basic substances (mainly pyridine bases) are removed from it by shaking with dilute sulphuric acid (1 : 30). The residual oil contains nitriles of the fatty acids (from propionic acid to stearic acid), which can be saponified by boiling with pulverized caustic alkali, together with benzene hydrocarbons, pyrrol and its homologues (*Ber.*, 13, 65). Pyrrols, mainly with pyrocoll (p. 402) (*Ber.*, 14, 1108), are produced on distilling gelatine.

As pyrrol is not symmetrical in constitution, the replacement of hydrogen atoms gives rise to different isomerides. The hydrogen atoms here, as in benzene, can be distinguished by means of numbers:—



The positions 1 and 4 are similar, and 2 and 3; the former can be called  $\alpha$ -, the latter  $\beta$ -positions. Carbopyrrolic acid,  $C_4H_3(NH).CO_2H$ , derived from pyromucic acid, has the carboxyl group in the  $\alpha$ -position.

**Methyl Pyrrols**,  $C_4H_3(NH).CH_3$ , Homopyrrols. Both isomerides, the  $\alpha$ - and  $\beta$ -, occur in that portion of Dippel's oil boiling between  $140$ – $150^\circ$ , but they cannot be separated. When fused with alkali they afford corresponding pyrrol carboxylic acids (see below). They may be obtained in a pure condition by withdrawal of the carboxyl group from the corresponding methyl-pyrrol carboxylic acids,  $C_4H_2(NH) \begin{array}{l} \diagup CH_3 \\ \diagdown CO_2H \end{array}$ .  $\alpha$ -Methyl Pyrrol boils at  $147$ – $148^\circ$ ,  $\beta$ -

**Methyl Pyrrol at  $142$ – $143^\circ$ .**

**Dimethyl Pyrrol**,  $C_4H_2(NH)(CH_3)_2$ , boiling at  $165^\circ$ , and **Trimethyl Pyrrol**,  $C_4H(NH)(CH_3)_3$ , at  $180$ – $195^\circ$ , seem also to consist of two isomerides (*Ber.*, 14, 1342).

**$\alpha$ -Pyrrol Carboxylic Acid**,  $C_4H_3(NH)CO_2H$ , Carbopyrrolic Acid, is formed from its amide and anhydride—pyrocoll (see below); or by fusing  $\alpha$ -homopyrrol with caustic alkali, and by the action of  $CCl_4$  and alcoholic potash upon pyrrol, or by heating it with ammonium carbonate (*Ber.*, 17, 1439). It crystallizes from water in prisms, which show a metallic green color when dry, and melt in closed tubes at  $191^\circ$ . Lead acetate does not precipitate its aqueous solution. When rapidly heated it breaks up into  $CO_2$  and pyrrol. The *methyl-ester* melts at  $73^\circ$ , the *ethyl-ester* at  $39^\circ$ .



**Pyrocoll**,  $C_{10}H_6N_2O_2 = C_4H_3:N-CO \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \begin{smallmatrix} CO:N \\ C_4H_3 \end{smallmatrix}$ , the imide anhydride of the

preceding, is produced in the distillation of gelatine (p. 401) and is artificially prepared by heating carbopyrrolic acid with acetic anhydride (*Ber.*, 17, 103). It crystallizes in yellow leaflets, melting about  $268^\circ$ . It yields carbopyrrolic acid when it is boiled with potash. Bromine converts it into mono-, di-, and tetrabrompyrocoll. When it is heated with  $PCl_5$  perchlorpyrocoll,  $C_{10}Cl_6N_2O_2$ , and the octochloride,  $C_{10}Cl_6(Cl_8)N_2O_2$ , are produced. Zinc and acetic acid convert the latter into perchlorpyrrol,  $C_4Cl_4NH$ , and on boiling with dilute acetic acid we obtain the imide of dichloromaleic acid (p. 337). When pyrocoll is dissolved in nitric acid dinitropyrocoll results; sodium hydrate converts this into nitrocarbopyrrolic acid (*Ber.*, 15, 1082; 16, 2388). Carbopyrrolamide,  $C_4H_3(NH).CO.NH_2$ , is produced together with pyrrol when ammonium pyromucate is subjected to distillation. It forms shining needles, melting at  $173^\circ$ . Boiling baryta decomposes it into  $NH_3$  and carbopyrrolic acid.

**$\beta$ -Pyrrol Carboxylic Acid**,  $C_4H_3(NH).CO_2H$ , is produced on fusing  $\beta$ -methyl pyrrol with KOH, and by the action of  $CO_2$  upon pyrrol-potassium. It crystallizes in needles, melting at  $161-162^\circ$ . The aqueous solution is precipitated by sugar of lead.

Carbon dioxide acts on the sodium methyl pyrrols to change them to  $\alpha$ - and  $\beta$ -Methyl-pyrrol Carboxylic Acid,  $C_4H_2(NH) \begin{smallmatrix} \diagup CH_3 \\ \diagdown CO_2H \end{smallmatrix}$ ; the former melting at  $169.5^\circ$ , and the latter at  $142.4^\circ$ . When heated above their point of fusion they yield  $CO_2$  and corresponding methyl pyrrols.

**Pseudo-acetyl Pyrrol**,  $C_4H_3(NH).CO.CH_3$ , is formed together with acetyl pyrrol (p. 400) on heating pyrrol with acetic anhydride. It crystallizes from hot water in long needles, which fuse at  $90^\circ$ ; it boils at  $220^\circ$ , and readily volatilizes with steam. Boiling alkalis do not decompose it. Silver can replace the imide hydrogen in it. It forms an acetoxim with hydroxylamine.  $MnO_4K$  oxidizes it to a ketonic acid,  $C_4H_3(NH).CO.CO_2H$ , which melts at  $75^\circ$  (*Ber.*, 16, 2348; 17, 432).

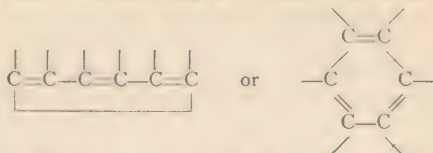
Nascent hydrogen transforms pyrrol into **Pyrrolin**,  $C_4H_5NH$ , hydromethylpyrrol. This is a liquid which dissolves easily in alcohol, and boils at  $90-91^\circ$ . It forms salts with acids, abstracts  $CO_2$  from the air, and is really a secondary base. Nitrous acid converts it into the nitroso-amine,  $C_4H_5N.NO$ ,—yellow needles, melting at  $37^\circ$ . The methyl pyrrolins are produced on heating it with methyl iodide (*Ber.*, 16, 1536).

## CLASS II.

### AROMATIC COMPOUNDS OR BENZENE DERIVATIVES.

The aromatic compounds are those substances which are mostly obtained from aromatic oils and resins. They differ in various respects from the members of the fatty or marsh gas series, but are principally distinguished by their greater carbon content. The theoretical representations upon their constitution are based chiefly on the views developed by Kekulé in 1865—Kekulé's *benzene theory*. All aromatic compounds are derived from a nucleus, comprising 6 carbon atoms; its simplest compound is found in

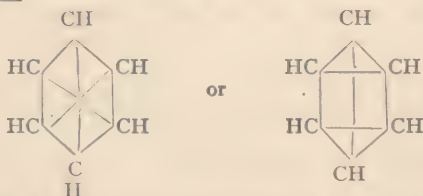
benzene,  $C_6H_6$ . The structure of this benzene nucleus is such that the 6 carbon atoms form a closed, ring-shaped chain, the atoms being joined alternately by single and double bonds, as follows :—



In benzene 1 hydrogen atom is attached to each of the 6 carbon atoms; all other aromatic compounds are derived by the replacement of the hydrogen, and may, therefore, be viewed as benzene derivatives.

The assumption of three double unions of carbon (same as in unsaturated fatty compounds) affords the simplest explanation for the power of the benzene derivatives to form addition products with 2, 4 and 6 atoms of chlorine, bromine or hydrogen (p. 411); it illustrates in the clearest manner the synthetic methods of producing derivatives of benzene, naphthalene, phenanthrene, etc.; it seems also that it must be inferred from the greater refractive power of the benzene derivatives. (p. 40).

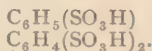
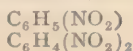
Another mode of representation assumes the grouping of the atoms so that in the benzene nucleus each carbon atom is attached singly to three other carbon atoms, as follows :—



According to this view there are nine single unions of carbon in benzene. The heat of combustion of the benzene compounds, apparently like that of the saturated fatty-bodies (*Thomsen, Ber.*, 13, 1808), may favor this view, and also the circumstance that the molecular volumes of benzene derivatives are less than those of the unsaturated compounds (p. 37). Yet, all chemical reactions, and especially all recent synthetic methods of producing the benzene nucleus argue for the existence of the double union of the carbon atoms. But, even according to the above assumption, the benzene nucleus is a closed chain composed of 6 carbon atoms.

The closed chain is characterized by great stability, being torn asunder or dismembered in chemical reactions with great difficulty. This is a property belonging to most all benzene derivatives. In external properties they are better characterized, are more readily crystallized, and are more reactive than the fatty compounds.

The halogens and the nitro- and sulpho-groups can readily replace the hydrogen of benzene :—



The *union* of the halogen atoms is much firmer in the benzene, than in the methane derivatives; as a general thing they cannot be exchanged for other groups by double decomposition. The production of *nitro-compounds* by the direct action of nitric acid is characteristic of the benzene derivatives, whereas the fatty compounds are generally oxidized and decomposed.

In the reduction of the nitro-derivatives we obtain the *amido-compounds* :—

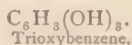
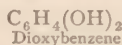
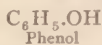


The so-called azo-derivatives appear as intermediate products of the reaction, whereas when nitrous acid acts on the amido-derivatives the diazo-compounds result. Both classes are of exceptional occurrence in the methane series (p. 130).

Benzene possesses a more negative character than the methane hydrocarbons. The phenyl group,  $\text{C}_6\text{H}_5$ , stands, as it were, between the positive alkyls,  $\text{C}_n\text{H}_{2n+1}$ , and the negative acid radicals. This is evident from the slight basicity of the phenylamines (like  $\text{C}_6\text{H}_5\cdot\text{NH}_2$ ), in comparison with the alkylamines. Diphenylamine,  $(\text{C}_6\text{H}_5)_2\text{NH}$ , is even a more feeble base, its salts being decomposed by water. Triphenylamine,  $(\text{C}_6\text{H}_5)_3\text{N}$ , is not capable of yielding salts.

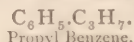
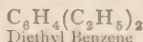
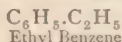
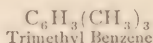
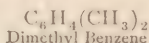
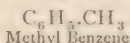
We discover the same in relation to the hydroxyl derivatives; these, unlike the alcohols, possess a more acidic character. The phenols (such as  $\text{C}_6\text{H}_5\cdot\text{OH}$ , carbolic acid) readily form metallic derivatives with basic hydroxides; trioxybenzene,  $\text{C}_6\text{H}_3(\text{OH})_3$  (Pyrogallic acid), reacts just like an acid.

By introducing OH into benzene for hydrogen we obtain the *phenols*, which may be compared to the alcohols :—

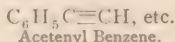
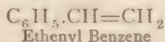


These resemble the tertiary alcohols in having the group C.OH attached to three carbon affinities (p. 88), hence on oxidation they cannot yield corresponding aldehydes, ketones or acids.

The entrance of hydrocarbon groups,  $\text{C}_n\text{H}_{2n+1}$ , in benzene produces the *homologues* of the latter :—



Unsaturated hydrocarbons also exist :—



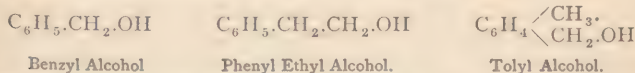
In these hydrocarbons the benzene residue preserves the specific properties of benzene; its hydrogen can readily be replaced by halogens and the groups  $\text{NO}_2$  and  $\text{SO}_3\text{H}$ . On the other hand, the side-chains behave like the hydrocarbons of the fatty series; their hydrogen can be replaced by halogens, but not by (by action of  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ) the groups  $\text{NO}_2$  and  $\text{SO}_3\text{H}$ . Different isomeric

derivatives are possible, depending upon whether the substitution of the halogens (or other groups) has occurred in the benzene residue or the side-chains, *e. g.* :—

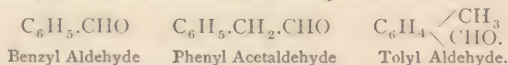


The halogen atoms in the benzene residue are very firmly combined and mostly incapable of double decomposition, while those in the side-chains react exactly as in the methane derivatives.

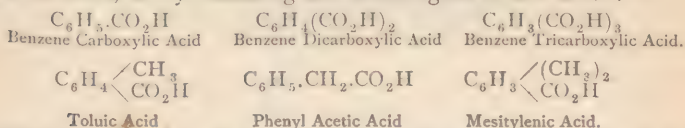
The substitution of hydroxyl for the hydrogen of the side-chains leads to the true alcohols of the benzene series :—



The *primary* class is oxidized to *aldehydes* and *acids* :—

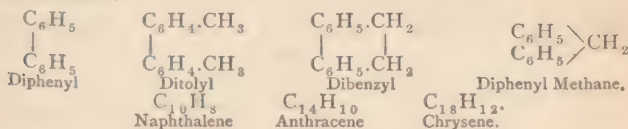


The acids can be formed by introducing carboxyl groups directly into benzene, or by oxidizing the homologues of the latter :—

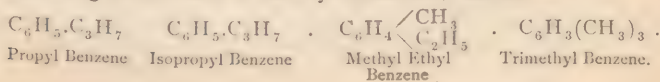


The hydrogen of the benzene residue in these acids, as well as in the alcohols and aldehydes, is replaceable by halogens, and the groups  $\text{NO}_2$ ,  $\text{SO}_3\text{H}$ ,  $\text{OH}$ , etc.

Furthermore, several benzene residues can unite directly, or through the agency of individual carbon atoms, forming higher hydrocarbons :—

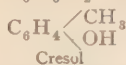


*Structure of the Isomerides.*—Numerous cases of isomerism are possible among the derivatives of benzene. One variety of isomerism corresponds exactly to that observed in the fatty series; it is founded in the isomerism of adjoining groups and their varying union with the benzene residue or in the side-chain. Thus we have the following isomerides of the hydrocarbon,  $\text{C}_9\text{H}_{12}$  :—

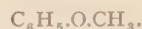
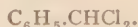




The compounds obtained by substitution in the benzene residue are isomeric with those derived by the same treatment of the side-chains :—

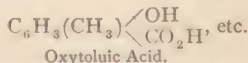
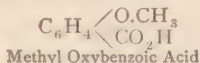
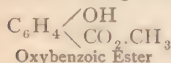


Benzyl Alcohol



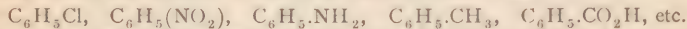
Phenyl Methyl Ether.

The following are also isomeric :—



Another kind of isomerism is based upon the structure of the benzene nucleus, and is conditioned by the relative positions of the substituting groups, hence it is designated *isomerism of position or place*.

All facts known at present argue with much certainty in favor of the *symmetrical structure* of benzene, that is, that the six hydrogen atoms, or more correctly the six affinities of the benzene nucleus are *alike* (same as the four affinities of carbon). Let any one hydrogen atom in benzene be replaced by another atom, or atomic group, and every resulting compound can exist in but one modification; thus there is but *one* chlorbenzene, one nitrobenzene, one amidobenzene, one toluene, one benzoic acid, etc. The following compounds are known in but one modification :—



The similarity of the six affinities is indicated not only by the fact that no mono-derivatives,  $\text{C}_6\text{H}_5\text{X}$ , can be prepared in more than one modification, but it can be directly proved. Thus in benzene four different hydrogen atoms (1, 2, 3, 4) are replaced by hydroxyl; in each case but one and the same phenol,  $\text{C}_6\text{H}_5.\text{OH}$ , results (*Ber.*, 7, 1684). And since two similar ortho- and meta positions exist in benzene ( $2 = 6$  and  $3 = 5$ , p. 408) all six affinities of the benzene nucleus must be equivalent.

Owing to this symmetry of the benzene nucleus, consisting of six carbon atoms, it can be represented by a regular hexagon; the numbers represent the six affinities, which in benzene compounds are saturated by other atoms or other groups.\*

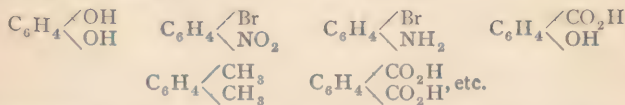
Now, although the six hydrogen atoms in benzene are similar, it is obvious from the graphic representation that every di-derivative,  $\text{C}_6\text{H}_4\text{X}_2$ , can exist in

\* The graphic formulas pictured on p. 403, representing the benzene nucleus, do not fully express the similarity of the six affinities, because according to them

the combinations  $\begin{array}{c} -\text{CX} \\ || \\ -\text{CX} \end{array}$  and  $\begin{array}{c} =\text{CX} \\ | \\ =\text{CX} \end{array}$  appear to be different. It has, however, been

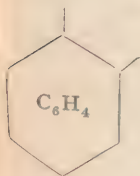
shown that they are identical (p. 408). The structural formulas only afford an approximate representation of the relations of isomerism, but do not express the real arrangement or position of the atoms, of which we are perfectly ignorant (p. 26). In the hexagon, however, their equivalence is fully expressed.

three modifications; their isomerism is dependent upon or due to the relative position of the two substituting groups. Indeed, nearly all di-derivatives are known in *three modifications*, but none in more than three. Thus there are three dioxybenzenes, three bromnitrobenzenes, three oxybenzoic acids, three toluenes, three dimethylbenzenes, three dicarboxylic acids, etc. The following compounds are known in three modifications each:—

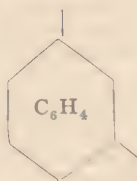


The compounds of the above series can be transformed into each other by various reactions; and, indeed, so that each of the three isomeric modifications (in normal reaction) is transformed into the corresponding modification of the other body. Three isomeric series of di-derivatives of benzene consequently exist; they are designated as the *ortho*, *meta*, and *para* series. We call all those *ortho*-compounds which belong to the series of phthalic acid; the *meta* or *iso*-compounds are those corresponding to isophthalic acid, and *para* those which correspond to parabrombenzoic acid and terephthalic acid.

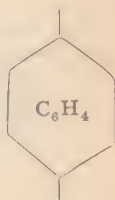
That an isomeric modification really belongs to one of the three series is determined in a purely empirical manner, either by directly or indirectly converting it into one of the three dicarboxylic acids,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$  (phthalic, isophthalic and terephthalic acid). The relative positions of the substituting groups in the benzene nucleus have, however, been ascertained with perfect certainty. In the *ortho*-compounds two adjoining hydrogen atoms in benzene are replaced (the positions 1 : 2 or 1 : 6; 1 here represents any one of the six similar hydrogen atoms); the *meta*-compounds have the structure, 1 : 3 or 1 : 5; whereas in the *para*-compounds, two opposite affinities (separated by two carbon atoms) are joined (positions 1 : 4). The following graphic representations will better explain the idea under consideration:—



Ortho-derivatives  
(1, 2)



Meta-derivatives  
(1, 3)



Para-derivatives.  
(1, 4)

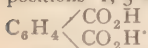
The following substances may be mentioned as chief representatives of the three isomeric series:—

	(1, 2)	(1, 3)	(1, 4)
$C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown OH \end{smallmatrix}$	Pyrocatechin	Resorcin	Hydroquinone.
$C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown CO_2H \end{smallmatrix}$	Salicylic Acid	Oxybenzoic Acid	Paraoxybenzoic Acid.
$C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown CH_3 \end{smallmatrix}$	Orthoxylene	Isoxylene	Paraxylene.
$C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown CO_2H \end{smallmatrix}$	Phthalic Acid	Isophthalic Acid	Terephthalic Acid.

The reason for supposing that the isomeric di-derivatives possess a structure such as indicated are:—

(1) Phthalic acid is obtained by the oxidation of naphthalene, and the structure of the latter (see this) is very probably such that the two carboxyl groups in the acid resulting from it can only have the position (1, 2) (Graebe).

(2) The structure of mesitylene,  $C_6H_3(CH_3)_3$ , is symmetrical; the three methyl groups present in it hold the positions 1, 3, 5 (see p. 410). The formation of mesitylene by the condensation of three molecules of acetone (*A. Bayer*) proves this; the substitutions of mesitylene (*Ladenburg, Ber., 7, 1133*) also indicate it with great certainty. The production of uvitic acid by the condensation of pyroracemic acid (p. 410) argues for the view that in it, and consequently also in mesitylene, the three side groups hold the positions (1, 3, 5). If we replace a  $CH_3$ -group in mesitylene by hydrogen we obtain isoxylene, called dimethyl benzene,  $C_6H_4(CH_3)_2$ , in which the two methyl groups can only have the positions 1, 3 = 1, 5. When isoxylene is oxidized it affords isophthalic acid,



(3) It is apparent on examining the benzene hexagon that only a *single position* (4 with reference to 1) is possible for the para-position while two similar positions can exist for the meta- and ortho-derivatives (the positions 3 and 5 and 2 and 6). This can be shown experimentally. It has been proved that the positions 3 and 5 are similar with reference to 1, consequently the meta-derivatives (1, 3) and (1, 5) are identical (*Ann., 192, 206, 222, 68*). In the same manner the ortho-derivatives (1, 2) and (1, 6) are identical, consequently the positions 2 and 6 are similar (*Ber., 2, 141* and *Ann., 192, 213*)—while the para-position occurs but once in the benzene nucleus (see *Berichte, 10, 218*). It has been shown that paraoxybenzoic acid, parabromtoluene, and, therefore, also terephthalic occupy it.

In addition to the preceding we have another means of determining the position, and it leads to exactly the same conclusions. If we replace another hydrogen atom (by  $NO_2$ ) in a para compound, (*e. g.* paradibrombenzene,  $C_6H_4Br_2$ ) it is evident from the figure that but one compound can result, one nitroparadibrombenzene—because the positions 2, 3, 5 and 6 (those which the  $NO_2$  can enter) are alike with reference to the para position, 1, 4. But 3 isomeric mononitro-derivatives are possible from metadibrombenzene (1, 3); in these the  $NO_2$  group occupies the positions 2, 4 (= 6) or 5. Orthodibrombenzene (1, 2) finally can yield 2 mononitro-derivatives; in these the  $NO_2$  group holds the positions

3(=6) and 4(=5). Therefore, six isomeric nitrodibrombenzenes,  $C_6H_3 \begin{smallmatrix} \diagup NO_2 \\ \diagdown Br_2 \end{smallmatrix}$ , are possible; 1 derived from the para, 3 from the meta, and 2 from ortho-dibrombenzene; conversely, by the retrogressive substitution of H for  $NO_2$  we discover that paradibrombenzene is afforded by but one nitrodibrombenzene; metadibrombenzene by three other nitrodibrombenzenes, and the ortho-compound by two nitrodibrombenzenes. Körner executed this method of ascertaining position with much satisfaction and certainty with the isomeric tribrombenzenes *Gazzetta chimica ital.*, IV, 305.) The study of the six isomeric nitro- (or amido-) benzoic acids,  $C_6H_3 \begin{smallmatrix} \diagup CO_2H \\ \diagdown (NO_2)_2 \end{smallmatrix}$ , afforded the same results (*Griess, Ber.* 5, 192 and 7, 1223).

That two adjacent carbon atoms of the benzene nucleus carry the side-groups in the ortho compounds is further concluded from their ability to yield so-called condensations and various anhydrides (compare the phenyl diamines, thioanilines, coumarines, indols, phthalic acid anhydrides, etc). There are also crystallographic grounds favoring the idea that the meta-compounds stand between those of the ortho and para series (*Zeitschrift f. Kryst.*, 1879, 171).

The benzene hexagon not only expresses all the relations of isomerism of the benzene derivatives, but also abundantly illustrates their chemical and physical deportment.

If three or more hydrogen atoms be replaced, two cases arise: the substituting groups are like or unlike. In the first instance three isomerides of the tri-derivatives, like  $C_6H_3(CH_3)_3$ , are possible, and they occupy the positions:—

(1, 2, 3) (1, 2, 4) and (1, 3, 5).

We call them *adjacent* (1, 2, 3), *unsymmetrical* (1, 2, 4), and *symmetrical* (1, 3, 5) tri-derivatives.

Three isomeric structural cases exist likewise for the tetra-derivatives, with four similar groups,  $C_6H_2X_4$  (analogous to the di-derivatives):—

(1, 2, 3, 4) (1, 2, 4, 5) and (1, 2, 3, 5).  
Adjacent Symmetrical Unsymmetrical.

Only one modification is possible when there are five and six similar groups; thus there exists but one pentachlorobenzene,  $C_6HCl_5$ , and but one hexachloride,  $C_6Cl_6$ .

When the substituting groups are unlike, the number of possible isomerides is far greater; they can easily be derived from the hexagon scheme. Thus, six isomeric modifications correspond to the formula of dinitrobenzoic acid,  $C_6H_3(NO_2)_2.CO_2H$ :—

(1, 2, 3) (1, 2, 4) (1, 2, 5) (1, 2, 6) (1, 3, 4) (1, 3, 5);

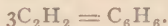
here the carboxyl group occupies position 1.

*Formation of Benzene Derivatives.*—The compounds of benzene can only be obtained in exceptional cases from methane derivatives by synthetic reactions.

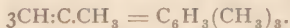
As they are generally very stable on exposure to heat (especially



the hydrocarbons and anilines), they are quite often produced by application of red heat to the methane derivatives. Thus benzene and other hydrocarbons result by heating acetylene strongly :—



Symmetrical trimethyl benzene (mesitylene) is similarly obtained from allylene,  $\text{CH}_3\cdot\text{C}:\text{CH}$ , on distilling its sulphuric acid solution :

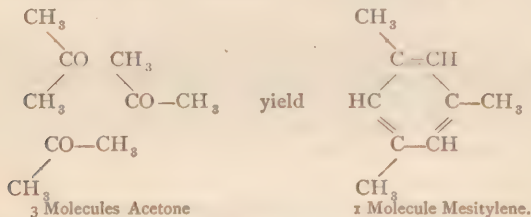
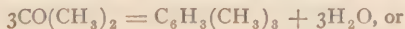


The polymerization of crotonylene,  $\text{CH}_3\cdot\text{C}:\text{C}:\text{CH}_3$  (p. 63), occurs even more readily, since shaking it with sulphuric acid suffices for its conversion into hexamethyl benzene,  $\text{C}_{12}\text{H}_{18}$  (*Ber.*, **14**, 2073) :



Mesitylene and cymene (methyl-propyl benzene) can be formed from divalerylene,  $\text{C}_{10}\text{H}_{16}$  (from valerylene,  $\text{C}_5\text{H}_8$ ), by decomposing the bromide with alkalis and heating with sulphuric acid.

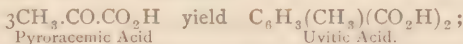
The formation of benzene compounds from ketones is very interesting ; the condensation here is probably analogous to that of crotonaldehyde from aldehyde (p. 154), and mesityl oxide from acetone (p. 165). Symmetrical trimethyl benzene (mesitylene) is formed rather abundantly on distilling acetone with sulphuric acid :



We can obtain in a similar manner symmetrical triethyl benzene,  $\text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_3$ , from methyl-ethyl ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_2\text{H}_5$ , tripropyl benzene,  $\text{C}_6\text{H}_3(\text{C}_3\text{H}_7)_3$ , from methyl-propyl ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_3\text{H}_7$ , and triphenyl benzene,  $\text{C}_6\text{H}_3(\text{C}_6\text{H}_5)_3$ , from methyl-phenyl ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ .

On heating phorone with sulphuric acid mesitylene (with acetone) is produced, but if  $\text{P}_2\text{O}_5$  or  $\text{ZnCl}_2$  be employed pseudocumene is the product.

The formation of uvitic acid,  $\text{C}_9\text{H}_8\text{O}_4$ , by boiling pyraccemic acid with baryta, is founded upon a like ketone-condensation :—



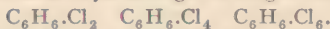
and so, too, is that of oxyuvitic acid,  $\text{C}_6\text{H}_2(\text{CH}_3)\left\{ \begin{array}{l} \text{OH} \\ (\text{CO}_2\text{H})_2 \end{array} \right.$ , in the action of sodium aceto-acetic ester upon chloroform (see *Ann.*, **222**, 258).

When the succino-succinic esters (p. 224) are heated with alkalis the products

are hydroquinone,  $C_6H_4(OH)_2$ , and hydroquinone dicarboxylic acid,  $C_6H_2(OH)_2(CO_2H)_2$ .

Again, when hexyl iodide,  $C_6H_{13}I$ , is heated with iodine chloride we get  $C_6Cl_6$ , or with bromine to  $200^\circ$ , perbrombenzene,  $C_6Br_6$ . Tetrabrom-methane,  $CBr_4$ , also affords  $C_6Br_6$  by raising it to  $300^\circ$ , when it parts with bromine.

*Addition Products.* Many benzene derivatives are able to combine directly with 2, 4 and 6 atoms of chlorine, bromine, hydrogen, etc. Here the three double bonds of the carbon atoms, as in the ethylenes, in all probability, change to single bonds:—



These addition products contain the ring-shaped, closed benzene chain, and are the compounds,  $C_6X_{12}$ , no longer able to saturate additional affinities. When the benzene ring is broken, hexane derivatives,  $C_6X_{14}$  are produced. The addition products are, therefore, true benzene derivatives, and can readily be converted into the normal compounds,  $C_6X_6$  (p. 414). The benzene ring is only broken in very energetic reactions, and then several products, like  $CO_2$  and acetic acid, are usually produced.

The decomposition of protocatechuic acid, pyrocatechin and allied bodies, by nitrous acid, into tetra-oxysuccinic acid (p. 378), and that of benzene, by chloric acid, into trichloroacetic acid and maleic acid (*Ann.*, 223, 170) are especially noteworthy.

### HYDROCARBONS, $C_nH_{2n-6}$ .

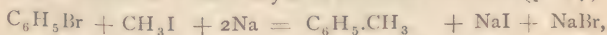
The benzene homologues are formed by substituting alkyls in benzene for hydrogen:—

$C_6H_6$ Benzene B. P. $80.5^\circ$	$C_6H_5.CH_3$ Toluene 110°	$C_6H_4(CH_3)_2$ Xylenes 137–140°	$C_6H_3(CH_3)_3$ Trimethyl Benzenes 163–166°	$C_6H_2(CH_3)_4$ Durene. 190°.
$C_6H_5.C_2H_5$ Ethyl Benzene 134°	$C_6H_5.C_3H_7$ Propyl Benzene 157°	$C_6H_5.C_4H_9$ Isopropyl Benzene 151°	$C_6H_5.C_4H_9$ Isobutyl Benzene. 163°.	

The entrance of the methyl group into the benzene nucleus elevates the boiling point about  $29-26^\circ$ ; its introduction in the side-chain causes an increase of about  $23-19^\circ$ . The boiling points of isomerides of position (p. 406) usually lie near each other; the ortho-compounds boil about  $5^\circ$ , and the meta-  $1^\circ$  higher than the para-derivatives.

*Preparation.*—The most important methods of preparing the benzene hydrocarbons are the following:—

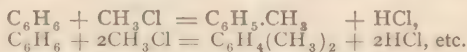
(1) Action of sodium upon mixtures of their bromides, and the bromides or the iodides of the alkyls in ethereal solution (p. 47):—



In carrying out these syntheses mix the bromide with the alkyl iodide and ether (free of water and alcohol), then add metallic sodium in thin pieces and allow to stand for some time, after which the whole is heated with a return condensed upon a water bath. A few drops of acetic ether sometimes accelerates the reaction. Para- and ortho-derivatives, *e. g.*,  $C_6H_4Br.CH_3$  and  $C_6H_4Br_2$ , react most readily. With the meta-compounds, which are not so easily attacked, bromides are substituted for alkyl iodides, or else benzene iodides are employed.

(2) Action of the alkylogens upon benzene hydrocarbons in the presence of aluminium chloride (zinc or ferric chloride)—*Friedel and Crafts*.

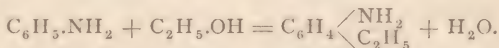
It is very likely that in this reaction metallo-organic compounds, *e. g.*,  $C_6H_5.Al_2Cl_5$ , are formed, which afterwards act upon the alkylogens:—



Even hexamethyl benzene,  $C_6(CH_3)_6$ , can be prepared after this manner. Various halogen derivatives, *e. g.*, chloroform (see diphenyl methane) and acid chlorides (see ketones) react similarly with the hydrocarbons of the benzene series.

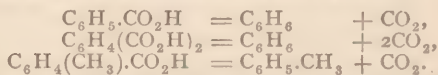
To effect syntheses after this style,  $AlCl_3$  ( $\frac{1}{3}$ – $\frac{1}{2}$  part) is added to benzene, and  $CH_3Cl$  or  $C_2H_5Cl$  is conducted into the heated mixture; or  $AlCl_3$  can be added to the benzene compound mixed with the chloride or bromide, and heat then applied until the evolution of  $HCl$  has almost ceased (*Ber.*, 16, 1745). The product is warmed with water and soda, and the oil which separates is subjected to distillation. Consult *Ber.*, 14, 2624, upon the introduction of methyl into homologous benzenes. The action of  $AlCl_3$  is very complicated; it frequently proceeds in other directions, and decompositions then ensue (*Ber.*, 15, 1451, 16, 169). A table of all the syntheses effected by  $AlCl_3$  may be found in *Ann., Chim. Phys.*, (6) I, 449.

The benzene nucleus may be alkylized if the  $HCl$  salts of alkylic anilines be heated alone, or if the anilines and methyl alcohol be heated to  $250$ – $300^\circ$ ; here the  $NH_2$  group is eliminated (*Ber.*, 13, 1729); or the anilines and fatty alcohols can be heated with zinc chloride to  $250^\circ$  (*Ber.*, 16, 105):—



Homologues of phenol (see these) are produced by heating fatty alcohols, phenol and zinc chloride together. The easy formation of isobutyl benzene on heating benzene and isobutyl alcohol with  $ZnCl_2$ , deserves notice.

(3) Dry distillation of a mixture of aromatic acids with lime or soda-lime (p. 46); iron filings are introduced to accelerate the conduction of heat. All the carboxyl groups are split off in this reaction and the original hydrocarbons set free:—



(4) Heating the oxygen derivatives, *e. g.*, phenols and ketones, with zinc dust, or with hydriodic acid and phosphorus. It is

remarkable, that benzophenone,  $C_6H_5.CO.C_6H_5$ , for example, is readily reduced, while the opposite is true of diphenyl ether,  $C_6H_5.O.C_6H_5$ .

(5) The methods of obtaining benzenes synthetically from fatty compounds, especially acetylenes and ketones, has already received notice (p. 410).

(6) Dry distillation of various, non-volatile carbon compounds, *e. g.*, wood, resins, bituminous shales, and especially bituminous coal. When the vapors of volatile methane derivatives ( $CH_4$ , alcohol, ether) are conducted through tubes heated to redness, they set free hydrogen and yield acetylene, benzene and its homologues, styrolene,  $C_8H_8$ , naphthalene,  $C_{10}H_8$ , anthracene, etc. Petroleum and the tar from lignite, containing ethane hydrocarbons, do the same.

The chief and almost exclusive material in preparing benzene hydrocarbons is coal tar, which is made in such large quantities in the manufacture of gas. Distillation divides the tar into a *light* and *heavy* oil. The former boils from  $60-180^\circ$  and contains principally benzene, toluene, xylene and trimethyl benzenes. As to their formation see *Ber.*, **10**, 854, **11**, 1213. To isolate the hydrocarbons, shake the light oil first with sulphuric acid, then with potash; wash, dry and finally fractionate over sodium. The heavy oil, boiling from  $160-220^\circ$ , sinks in water and comprises mainly phenol, cresol, aniline and naphthalene. In the portions of coal tar boiling at high temperatures, we have the solid hydrocarbons; naphthalene,  $C_{10}H_8$ , acenaphthene,  $C_{12}H_{10}$ , anthracene and phenanthrene,  $C_{14}H_{10}$ , pyrene,  $C_{16}H_{10}$ , chrysene,  $C_{18}H_{12}$ , and others. Some benzene hydrocarbons occur already formed in small amount in the naphtha varieties (p. 52) (for their recognition by means of bromine and  $AlBr_3$ , see *Ber.*, **16**, 2265), and in different ethereal oils (together with aldehydes, alcohols and acids).

Phenols, benzene, and its homologues (see *Cymene*, p. 419) are obtained by distilling camphor with zinc chloride, or phosphorus sulphide.

*Properties.* The hydrocarbons of the benzene series are volatile liquids, insoluble in water, but soluble in alcohol and ether; some, containing only methyl groups, are solids at ordinary temperatures. They dissolve in concentrated sulphuric acid, on application of heat, to form sulphonic acids, *e. g.*,  $C_6H_5.SO_3H$ , from which the hydrocarbons can be reformed by dry distillation or by heating with concentrated hydrochloric acid to  $150-180^\circ$ . The best course would be to distil the ammonium sulphonates, or the mixture of lead salts with ammonium chloride (*Ber.*, **16**, 1468). This reaction is the basis of a method for the separation of the benzenes and marsh gas series; it also permits of the preparation of the former in pure form. The benzenes dissolve in concentrated nitric acid, forming nitro-derivatives.



Acids are produced (aromatic acids) by oxidizing the side-chain of homologous benzenes with nitric acid, a chromic acid mixture, potassium permanganate, or ferricyanide of potassium. Energetic oxidation converts benzene into  $\text{CO}_2$ ; only minute quantities of benzoic and phthalic acid are formed at the time.

Chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , unites with the benzene homologues to form compounds which water converts into aromatic aldehydes (see these).

When heated with concentrated hydriodic acid or phosphonium iodide,  $\text{PI}_4\text{I}$ , to about  $300^\circ$ , the benzene hydrocarbons yield hydrogen addition products (p. 411); thus with  $\text{PI}_4\text{I}$  toluene yields  $\text{C}_7\text{H}_8\cdot\text{H}_2$ , isoxylene,  $\text{C}_8\text{H}_{10}\cdot\text{H}_4$ , and mesitylene, the hexahydride,  $\text{C}_9\text{H}_{12}\cdot\text{H}_6$ , while all the benzenes when acted on with much hydriodic acid finally yield the hexahydrides,  $\text{C}_n\text{H}_{2n}$ . These last compounds are the chief ingredients of Caucasian petroleum (p. 52). Oxidizing agents frequently separate the added hydrogen atoms, or the hydride is completely destroyed. They dissolve in fuming nitric acid to form nitro-derivatives of the normal benzenes,  $\text{C}_n\text{H}_{2n}-6$ .

1. **Benzene**,  $\text{C}_6\text{H}_6$ , contained in coal tar, is formed by the dry distillation of all benzene acids, having only  $\text{CO}_2\text{H}$  side groups (p. 412).

That portion of the coal tar boiling from  $80-85^\circ$  is chilled by means of a freezing mixture, and the solid benzene then pressed out in the cold. To get perfectly pure benzene, distil a mixture of benzoic acid (1 part) and  $\text{CaO}$  (3 parts).

Common benzene from coal tar, even the purified article, invariably contains thiophene,  $\text{C}_4\text{H}_4\text{S}$ ; hence it affords the indiofenin reaction (p. 398). When heated with sodium it gives the reaction of  $\text{Na}_2\text{S}$ . Concentrated sulphuric acid turns it brown, and when the acid contains  $\text{N}_2\text{O}_3$  the coloration is violet (*Ber.*, 16, 1473).

Benzene is a mobile, ethereal-smelling liquid, of specific gravity 0.899 at  $0^\circ$  (0.8799 at  $20^\circ$ ). It solidifies about  $0^\circ$ , melts at  $+6^\circ$ , and boils at  $80.5^\circ$ . It burns with a luminous flame, mixes with absolute alcohol and ether, and dissolves resins, fats, sulphur, iodine and phosphorus readily.

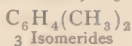
**Benzene Hexahydride**,  $\text{C}_6\text{H}_6\cdot\text{H}_6$  (see above), boils at  $69^\circ$ ; its specific gravity at  $0^\circ$  is 0.76.

2. **Toluene**,  $\text{C}_7\text{H}_8 = \text{C}_6\text{H}_5\cdot\text{CH}_3$ , is obtained from coal tar, and is produced in the dry distillation of tolu balsam and many resins. It is synthetically prepared by the action of sodium upon  $\text{C}_6\text{H}_5\text{Br}$  and  $\text{CH}_3\text{I}$ , and by the distillation of toluic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH}_3 \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$ , with lime. It is very similar to benzene, boils at  $110.3^\circ$ , and has a specific gravity at  $0^\circ$  of 0.882 (0.8656 at  $20^\circ$ ). It does not solidify at  $-28^\circ$ . Dilute nitric acid and chromic acid oxidize it to benzoic acid; chromyl chloride converts it into benzaldehyde.

Ordinary, not perfectly pure, toluene contains some thiophene, hence affords the anthraquinone reaction (p. 399).

**Toluene Dihydride**,  $C_7H_8.H_{12}$ , boils at  $185-208^\circ$ . **Toluene Hexahydride**,  $C_7H_8.H_6$ , boils at  $97^\circ$ ; sp. gr. 0.772 at  $0^\circ$ .

### 3. Hydrocarbons, $C_8H_{10}$ :—



The three dimethyl benzenes,  $C_6H_4(CH_3)_2$ , or methyl toluenes (ortho, meta and para), are called

**Xylenes**, and occur in coal tar. Orthoxylene, with a little of the para variety, is produced on conducting  $CH_3Cl$  into benzene or toluene containing  $AlCl_3$  (p. 412) (*Ber.*, 14, 2627).

That portion of coal tar oil boiling between  $136-141^\circ$  contains, in addition to ten per cent. paraffins, variable quantities of metaxylene (as much as 85 per cent.), paraxylene (as high as 20 per cent.), and orthoxylene (up to 20 per cent.). When the mixture is boiled with dilute nitric acid (1 part  $NO_3H$  and 3 parts  $H_2O$ ) the ortho- and para- varieties are oxidized to their corresponding toluic acids,  $C_6H_4(CH_3).CO_2H$ , while metaxylene and the paraffins are unattacked. On shaking crude xylene with ordinary sulphuric acid, the ortho- and meta- xylenes dissolve to form sulphonic acids; sodium orthoxylenesulphonate is difficultly soluble in water. Paraxylene is only soluble in fuming sulphuric acid. It also volatilizes first when crude xylene is distilled with steam (*Ber.*, 10, 1013; 14, 2625; 17, 444).

**Orthoxylene** (1, 2) is obtained from orthobrom-toluene by means of  $CH_3I$  and sodium, and can be prepared from toluene by means of  $CH_3Cl$  and  $AlCl_3$  (*Ber.*, 14, 2628). It boils at  $142-143^\circ$ . Dilute nitric acid oxidizes it to ortho-toluic acid,  $C_6H_4(CH_3).CO_2H$ ; chromic acid decomposes it into  $CO_2$ , and with potassium permanganate it affords ortho-toluic and phthalic acids.

Ortho-xylene can be nitrated by heating it for some time (6-8 hours) with a mixture of  $NO_3H$  and  $SO_4H_2$ . Bromine, at  $150^\circ$ , converts it into ortho-xylene bromide,  $C_6H_4(CH_2Br)_2$ , which melts at  $93^\circ$  (*Ber.*, 17, 123). *Ortho-xylene chloride*,  $C_6H_4(CH_2Cl)_2$ , has been obtained from phthalyl alcohol.

**Metaxylene**, or Isoxylene (1, 3), is obtained from coal tar, and is produced from mesitylene,  $C_6H_3(CH_3)_3$  (1, 3, 5), by heating mesitylenic acid,  $C_6H_3(CO_2H)_3$ , with lime. It could not be prepared from metabromtoluene,  $C_6H_4Br.CH_3$ , but was gotten in small quantity from meta-iodo-toluene. It boils at  $137^\circ$ ; its specific gravity at  $0^\circ$  is 0.878. It is not oxidized by ordinary nitric acid until heated to  $130^\circ$ . It is attacked more energetically by a chromic acid mixture than the para variety and yields isophthalic acid,  $C_6H_4(CO_2H)_2$ . The hydrides are obtained by heating it with  $H_2$  or  $PH_4I$ :  $C_8H_{10}.H_4$  and  $C_8H_{10}.H_6$ , the latter boils at  $118^\circ$ , and when acted upon with nitric and sulphuric acids affords trinitro-isoxylene.

When metaxylene is chlorinated at the boiling temperature meta-Tolyl-chloride,  $C_6H_4(CH_3).CH_2Cl$ , is formed; this boils at  $165^\circ$ .

On warming metaxylene with fuming nitric acid a dinitro-product results, which melts at  $93^\circ$ .  $SO_4H_2$  and  $NO_3H$  afford a trinitro-product,  $C_6H(NO_2)_3.(CH_3)_2$ ; this melts at  $176^\circ$ . Characteristic amido compounds are obtained by the reduction of the preceding nitro-derivatives. Cold, fuming nitric acid produces the mononitro-compound, which melts at  $+2^\circ$  and boils at  $237-239^\circ$ .

**Paraxylene** (1, 4) is formed when camphor is diluted with  $ZnCl_2$  and is obtained pure by the action of sodium and  $CH_3I$  upon parabromtoluene,  $C_6H_4Br.CH_3$ , or better, upon paradibrombenzene,  $C_6H_4Br_2$  (*Ber.*, 10, 1356). It boils

at 136–137°; its sp. gr. at 19° is 0.862. Pure paraxylene solidifies in the cold forming monoclinic needles, which melt at 15°. Dilute nitric acid oxidizes it first to paratoluic acid and subsequently to terephthalic acid,  $C_6H_4(CO_2H)_2$ . Chromic acid converts it immediately into the latter acid. With fuming nitric acid it yields two isomeric dinitro-paraxylenes,  $C_6H_2(NO_2)_2(CH_3)_2$ ; the first melting at 93°, the second, more difficultly soluble in alcohol, at 123.5°.  $NO_3H$  and  $H_2SO_4$  convert it into a trinitro-derivative,  $C_6H(NO_2)_3(CH_3)_2$ , which melts at 137°. The reduction of these compounds affords ill-defined amido-compounds. Paraxylene is soluble in fuming sulphuric acid only; its sulphonic acid forms large crystals, and is not very soluble.

**Ethyl Benzene**,  $C_6H_5.C_2H_5$ , is produced by the action of sodium upon  $C_6H_5Br$  and  $C_2H_5Br$ , of hydriodic acid upon styrolene,  $C_6H_5.C_2H_3$ , but best in the action of  $C_2H_5Cl$  and  $AlCl_3$  upon benzene. It boils at 134°. Its specific gravity at 22° equals 0.866. Dilute nitric acid and chromic acid oxidize it to benzoic acid;  $CrO_2Cl_2$  converts it into phenyl acetaldehyde,  $C_6H_4.CH_2.CHO$ . It gives two liquid mononitro-products,  $C_6H_4(NO_2).(C_2H_5)_2$  (1, 2) and (1, 4), by the action of fuming nitric acid. The first boils at 227°, the second at 245°.

In the heat chlorine converts it into  $\alpha$ -chloroethyl benzene.\* In the warm liquid, bromine forms  $\beta$ -bromethylbenzene,  $C_6H_5.CHBr.CH_3$ ; this is also prepared from phenylmethyl carbinol, by the action of  $HBr$ . Both compounds are liquids and on distilling, they decompose partly into  $HCl$  and styrolene. With potassium cyanide the  $\alpha$ -derivative affords a cyanide and then hydrocinnamic acid. The  $\beta$ -derivative reacts neither with  $CNK$ , nor with  $Na$  and  $CO_2$ ; with zinc dust and benzene it yields diphenyl ethane,  $(C_6H_5)_2CH.CH_3$ . The addition of  $HBr$  to styrolene,  $C_6H_5.CH:CH_2$  gives apparently  $\alpha$ -bromethyl benzene,  $C_6H_5.CH_2.CH_2Br$  (*Ber.*, 15, 1983).  $\alpha$ -Dichloroethyl benzene,  $C_6H_5.CH_2.CHCl_2$ , obtained from phenylacetaldehyde,  $C_6H_5.CH_2.CHO$ , by the action of  $PCl_5$ , is a very unstable, thick liquid, which passes into  $\alpha$ -chlorostyrolene (*Ber.*, 17, 982), when acted upon by alcoholic potash.  $\beta$ -Dichloroethyl benzene,  $C_6H_5.CCl_2.CH_2$ , is formed from acetophenone,  $C_6H_5.CO.CH_3$ .  $\alpha$ , $\beta$ -Dichloroethyl benzene,  $C_6H_5.CHCl.CH_2Cl$ , styrolene chloride, from chlorine and styrolene, affords  $\alpha$ -chlorostyrolene with alcoholic potash.

#### 4. Hydrocarbons, $C_9H_{12}$ .

$C_6H_3(CH_3)_3$   
Trimethyl Benzenes  
3 Isomerides

$C_6H_4 \left\{ \begin{array}{l} CH_3 \\ C_2H_5 \end{array} \right.$   
Methyl Ethyl Benzenes  
3 Isomerides

$C_6H_5.C_3H_7$   
Propyl Benzenes.  
2 Isomerides.

##### 1. Trimethyl Benzenes.

(1) **Mesitylene**, symmetrical trimethyl benzene,  $C_6H_3(CH_3)_3$  (1, 3, 5), occurs in coal tar, and is produced by distilling acetone or allylene with sulphuric acid; also prepared from phorone (p. 410).

*Preparation.*—Distil a mixture of acetone (1 volume) and sulphuric acid (1 volume) diluted with  $\frac{1}{2}$  volume water. It is well also to add some sand. The distillate consists of two layers; the upper, oily layer is siphoned off, washed with a soda solution and fractionated.

\*The  $\alpha$ -compounds are those derivatives in which the halogen atoms are attached to the first substituted carbon atom (of the side-chain) (p. 179) (*Ber.*, 17, 960).

Mesitylene is an agreeable-smelling liquid, which boils at  $163^{\circ}$ . When heated with dilute nitric acid the methyl groups are successively oxidized to mesitylenic acid, uvitic acid and trimesic acid,  $C_6H_3(CO_2H)_3$  (1, 3, 5). Chromic acid breaks it up, yielding acetic acid. Heated to  $280^{\circ}$  with  $PH_4I$  we get  $C_9H_{12}.H_6$ , boiling at  $138^{\circ}$ , and yielding the same products as mesitylene when oxidized.

*Nitromesitylene*,  $C_9H_{11}(NO_2)$ , is obtained by the nitration of mesitylene in glacial acetic acid; it melts at  $44^{\circ}$ . *Dinitromesitylene* melts at  $86^{\circ}$ . The *trinitro-compound*, obtained by adding mesitylene to a cold mixture of  $NO_3H$  and  $SO_4H_2$ , crystallizes from benzene in large, colorless needles. It dissolves in hot alcohol, but not readily in ether, and melts at  $232^{\circ}$ .

$C_6H_2Cl(CH_3)_3$  boils at  $205^{\circ}$ .  $C_6HCl_2(CH_3)_3$  melts at  $59^{\circ}$ , and boils at  $244^{\circ}$ .  $C_6Cl_3(CH_3)_3$  melts at  $204^{\circ}$ .  $C_6H_2Br(CH_3)_3$  solidifies at  $0^{\circ}$  and boils at  $225^{\circ}$ .  $C_6HBr_2(CH_3)_3$  melts at  $60^{\circ}$ ,  $C_6Br_3(CH_3)_3$  at  $224^{\circ}$ .

The symmetrical structure of mesitylene renders it impossible to have isomerides in these substitution products (*Ann.*, 179, 163).

(2) **Pseudocumene**,  $C_6H_3(CH_3)_3$  (1, 3, 4), unsymmetrical trimethyl benzene, occurs with mesitylene in coal tar (boiling at  $162-168^{\circ}$ ) in about equal amount. It cannot, however, be separated by fractional distillation.

To separate these two hydrocarbons, dissolve the mixture in concentrated sulphuric acid and dilute with water, when the more difficultly soluble cumene-sulphonic acid will separate in the form of crystals, while mesitylene-sulphonic acid continues in solution (*Ber.*, 9, 258). The hydrocarbons are obtained by heating the sulpho-acids with hydrochloric acid to  $175^{\circ}$  (p. 413).

It may be synthesized by the action of sodium and  $CH_3I$  upon bromparaxylene (1, 4) and brom-metaxylene (1, 3), hence the structure (1, 3, 4). It appears in small quantities when phorone is heated with  $P_2O_5$  or  $ZnCl_2$ . Pseudocumene boils at  $166^{\circ}$ . Nitric acid oxidizes it to xylic acid, so-called paraxylic acid, and finally to xyllic acid,  $C_6H_3(CH_3)(CO_2H)_2$  (see these).

A mixture of  $NO_3H$  and  $H_2SO_4$  converts pseudocumene into a *trinitro-compound*,  $C_6(NO_2)_3(CH_3)_3$ , which is not very soluble in alcohol, but crystallizes from benzene in thick prisms, melting at  $185^{\circ}$ . The gradual addition of bromine to cold pseudocumene results in the formation of a crystalline *monobromide* (melting at  $73^{\circ}$ ); the addition of any more reagent makes the product liquid, and it finally becomes the solid tribromide,  $C_6Br_3(CH_3)_3$ , melting at  $224^{\circ}$ .

When crude pseudocumene, from coal tar, is poured into a mixture of fuming  $NO_3H$  and  $SO_4H_2$  a crystalline mass is formed; it contains three trinitro-cumenes. Crystallized from benzene the mesitylene derivative separates first in long needles, then follows the pseudocumene in thick prisms.

(3) **Hemimellitene**,  $C_6H_3(CH_3)_3$  (1, 2, 3), adjacent trimethyl benzene, is obtained from  $\alpha$ -isodurylic acid,  $C_6H_2(CH_3)_3.CO_2H$ , and boils at  $168-170^{\circ}$ ; it is not contained in coal tar.

2. **Ethyl Toluenes**,  $C_6H_4 \begin{Bmatrix} CH_3 \\ C_2H_5 \end{Bmatrix}$ . The (1, 4) compound, from parabrom-toluene, boils at  $161-162^{\circ}$ , and when oxidized yields paratoluic and terephthalic acids. The (1, 3) ethyl toluene, from metabrom-toluene, boils near  $150^{\circ}$ ; its sp. gr. at  $20^{\circ}$  is 0.869. It yields isophthalic acid on oxidation.

3. **Propyl Benzenes**,  $C_6H_5.C_3H_7$ . Normal propyl benzene, obtained from  $C_6H_5Br$ , propyl iodide or bromide and sodium, or from benzyl chloride,  $C_6H_5.CH_2Cl$ , by the action of zinc ethide, boils at  $157^{\circ}$ ; its specific gravity is 0.881 at  $0^{\circ}$ . In the cold bromine converts it into parabrom-propyl benzene,  $C_6H_4Br.C_3H_7$ , boiling at  $220^{\circ}$ . Normal cumic acid is obtained from this by the action of

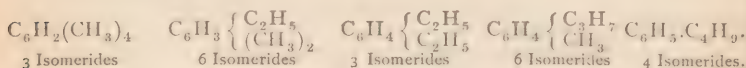


sodium and  $\text{CO}_2$  (*Ber.*, 15, 698). If it be treated while hot, with bromine, we get  $\beta\gamma$ -dibrom-propyl benzene,  $\text{C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CH}_3$  (*Ber.*, 17, 709). Propyl benzene yields phenyl-propionic aldehyde,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$ , when acted upon with chromyl chloride.

**Isopropyl Benzene**,  $\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_7$ , called **Cumene**, is made by distilling cumic acid with lime, and by the action of  $\text{AlBr}_3$  upon a mixture of benzene with isopropyl bromide or normal propyl bromide; in the latter instance the normal propyl group sustains a transposition (p. 67). Cumene boils at  $153^\circ$ ; its specific gravity is 0.879 at  $0^\circ$ . Parabrom-cumene,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}_3\text{H}_7$ , yields common cumic acid,  $\text{C}_6\text{H}_4(\text{C}_3\text{H}_7)\cdot\text{CO}_2\text{H}$ , with sodium and  $\text{CO}_2$ .

Nitric acid or the chromic acid mixture oxidizes both propyl benzenes to benzoic acid.

#### 4. Hydrocarbons, $\text{C}_{10}\text{H}_{14}$ :—



1. **Tetramethyl Benzenes**,  $\text{C}_6\text{H}_2(\text{CH}_3)_4$ . Symmetrical **Durene** (1, 2, 4, 5) is formed from brompseudo cumene,  $\text{C}_6\text{H}_2\text{Br}(\text{CH}_3)_3$ , and dibromisoxylene,  $\text{C}_6\text{H}_2\text{Br}_2(\text{CH}_3)_2$ , by means of  $\text{CH}_3\text{I}$  and sodium; and from toluene by  $\text{CH}_3\text{Cl}$  and  $\text{AlCl}_3$  (*Ann.*, 216, 200). It is crystalline, possesses a camphor-like odor, melts at  $79$ – $80^\circ$  and boils at  $190^\circ$ . Nitric acid oxidizes it to durylic and cumidic acids,  $\text{C}_6\text{H}_2(\text{CH}_3)_2\cdot(\text{CO}_2\text{H})_2$  (the symmetrical constitution of durene is concluded from this (*Ber.* 11, 31). *Dibromadurene* melts at  $199^\circ$ ; *dinitrodurene*,  $\text{C}_6(\text{NO}_2)_2(\text{CH}_3)_4$ , at  $205^\circ$ .

Unsymmetrical **Isodurene** (1, 3, 5,  $\text{CH}_3$ ) is obtained from brom-mesitylene with  $\text{CH}_3\text{I}$  and Na, and from mesitylene by means of  $\text{CH}_3\text{Cl}$  and  $\text{AlCl}_3$ . It boils at  $195^\circ$  and does not solidify in the cold. *Dibromisodurene* melts at  $209^\circ$ , *dinitroisodurene* at  $156^\circ$ . The oxidation of isodurene with nitric acid affords three isodurylic acids,  $\text{C}_6\text{H}_2(\text{CH}_3)_3\cdot\text{CO}_2\text{H}$  (*Ber.*, 15, 1853).

2. Symmetrical **Ethylidimethyl Benzene**,  $\text{C}_6\text{H}_3\left\{\begin{array}{l} (\text{CH}_3)_2 \\ \text{C}_2\text{H}_5 \end{array}\right\}$  (1, 3, 5), is produced (simultaneously with methyl diethyl benzene) by distilling a mixture of dimethyl ketone and methyl ethyl ketone with sulphuric acid (p. 410). It boils at  $185^\circ$  and is converted into mesitylenic and uvitic acids by nitric acid. *Methyl-diethyl Benzene*,  $\text{C}_6\text{H}_3\left\{\begin{array}{l} \text{CH}_3 \\ (\text{C}_2\text{H}_5)_2 \end{array}\right\}$ , which is formed at the same time, boils at  $198$ – $200^\circ$ .

(1, 2, 4)-**Ethylidimethyl Benzene** (Laurene) is obtained by heating camphor with  $\text{ZnCl}_2$  or iodine. It boils at  $189^\circ$  and is oxidized to paraxylic acid,  $\text{C}_6\text{H}_3(\text{CH}_3)_2\cdot\text{CO}_2\text{H}$ , by nitric acid (*Ber.*, 16, 2258).

3. **Diethyl Benzene**,  $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)_2$  (1, 4), obtained from para-bromomethyl benzene or paradibrom-benzene, boils at  $181^\circ$  and is oxidized to paraethyl-benzoic acid and terephthalic acid.

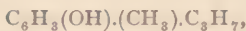
4. **Methylpropyl Benzenes**,  $\text{C}_6\text{H}_4\left\{\begin{array}{l} \text{CH}_3 \\ \text{C}_3\text{H}_7 \end{array}\right\}$ . Those of the six possible isomerides, having the normal propyl group, are designated *cymenes* and those with the isopropyl group, *isocymenes*.

**Orthocymene** (1, 2) is formed from orthobromtoluene and propyl iodide, by the action of sodium, and boils at  $181$ – $182^\circ$ .

**Metacymene** (1, 3) is formed from metabromtoluene and propyl iodide, and boils at  $176$ – $177^\circ$ . **Metaisocymene** (1, 3) occurs in resin and is formed from toluene and isopropyl iodide in the presence of  $\text{AlCl}_3$ . It boils at  $171$ – $175^\circ$  and

is oxidized to isophthalic acid by chromic acid. Consult *Ber.*, 16, 2748, for the sulphonic acids.

**Para-cymene**,  $C_6H_4 \left\{ \begin{smallmatrix} CH_3 \\ C_3H_7 \end{smallmatrix} \right.$  (1, 4), methyl normal propyl benzene. This is usually called **cymene** and occurs in Roman caraway-oil (from *Cuminum cyminum*), together with cumic aldehyde, and in other ethereal oils. It is produced on heating thymol and carvacrol,



with  $P_2S_5$ , or with  $PCl_5$  and sodium amalgam; also by heating camphor,  $C_{10}H_{16}O$ , and some of its isomerides with  $P_2S_5$  (along with meta-isocymene, *Ber.*, 16, 791 and 2258), or with  $P_2O_5$  (in pure state). (When camphor is heated with  $ZnCl_2$  it affords a series of benzene homologues, but, as it seems, no cymene, *Ber.*, 16, 624, and 2255). Cymene is obtained from turpentine oil and other terpenes,  $C_{10}H_{16}$ , by the withdrawal of two hydrogen atoms from them. This is effected by heating with  $SO_4H_2$  or, better, with iodine, or by the action of alkalis or aniline upon the dibromide,  $C_{10}H_{16}Br_2$ . Especially interesting is the production of cymene on boiling cumic alcohol,  $C_6H_4(C_3H_7).CH_2.OH$  (having the isopropyl group), with zinc dust. A transformation of the isopropyl group takes place. It may be synthetically prepared from parabrom-toluene,  $C_6H_4Br.CH_3$ , by means of normal propyl iodide and sodium.

*Preparation.*—Take a mixture of equal parts of camphor and  $P_2O_5$  and heat until the reaction ceases. The cymene produced is poured off, again boiled with a little  $P_2O_5$ , and then distilled over sodium (*Ann.*, 172, 307). Or, shake Roman caraway-oil with a concentrated sodium bisulphite solution, which also dissolves the cumic aldehyde contained in the oil. The oil is separated and then fractionated.

Cymene is a pleasantly-smelling liquid, that boils at  $175-176^\circ$ ; its specific gravity at  $0^\circ$  is 0.8722. It exhibits a characteristic absorption spectrum. It dissolves in concentrated sulphuric acid on warming, and forms a sulphonic acid. The characteristic barium salt,  $(C_{10}H_{13}SO_3)_2Ba + 3H_2O$ , crystallizes in shining leaflets.

Dilute nitric acid or the chromic acid mixture oxidizes cymene to paratoluic acid,  $C_6H_4(CH_3).CO_2H$ , and terephthalic acid; whereas in the animal organism or upon shaking with caustic soda and air it is, strange to say, converted into cumic acid,  $C_6H_4(C_3H_7).CO_2H$  (with the isopropyl group). The same oxypropyl-sulpho-benzoic acid,  $C_6H_3(C_3H_6.OH) \left\{ \begin{smallmatrix} CO_2H \\ SO_3H \end{smallmatrix} \right.$ , as that afforded by para-isocymene sulphonic acid, is produced by the action of  $MnO_4K$  upon cymene sulphonic acid (*Ber.*, 14, 1136).

**Para-isocymene** (1, 4) could not be made from parabrom toluene and isopropyl iodide, but is prepared from parabrom-cumene,  $C_6H_4Br.C_3H_7$ , by means of methyl iodide and sodium. It resembles paracymene in odor and boils at  $171-172^\circ$ ; its specific gravity is 0.870 at  $0^\circ$ .

5. **Butyl Benzenes**,  $C_6H_5.C_4H_9$ . *Normal butyl benzene* boils at  $180^\circ$ , *Isobutyl benzene* at  $167^\circ$ . They are obtained from brom-benzene by means of the

butyl bromides, and from benzyl chloride,  $C_6H_5.CH_2Cl$ , by propyl and isopropyl iodides. When benzene is quickly heated to  $300^\circ$  with isobutyl alcohol isobutyl benzene is formed (*Ber.*, 15, 1425). The *secondary butyl benzene*,  $C_6H_5.CH(CH_3)C_2H_5$ , is formed from  $\beta$ -bromomethyl benzene (p. 416) by means of zinc ethyl. It boils at  $171^\circ$ . The three butyl benzenes yield benzoic acid when they are oxidized.

The following higher benzene homologues may be mentioned :—

**Isomyl Benzene**,  $C_6H_5.C_5H_{11}$ , boils at  $193^\circ$ . **Secondary Amyl Benzene**,  $C_6H_5.CH(C_2H_5)_2$ , formed by the action of zinc ethyl upon  $C_6H_5.CHCl_2$ , boils at  $178^\circ$ .

**Symmetrical Triethyl Benzene**,  $C_6H_3(C_2H_5)_3$  (1, 3, 5), is made by distilling ethyl-methyl ketone,  $C_2H_5.CO.CH_3$ , with sulphuric acid (p. 410). It boils at  $218^\circ$ , and yields trimesic acid with chromic acid.

**Pentamethyl Benzene**,  $C_6H(CH_3)_5$ , is produced when  $AlCl_3$  and methyl chloride act upon benzene and toluene. It boils about  $230^\circ$ , crystallizes on cooling, and is soluble in concentrated sulphuric acid.

**Hexamethyl Benzene**,  $C_6(CH_3)_6 = C_{12}H_{18}$ , is formed, together with the preceding, by the polymerization of crotonylene,  $CH_3.C:C.CH_3$ , on shaking with sulphuric acid (p. 410), and by heating xylidene hydrochloride and methyl alcohol to  $300^\circ$  (p. 412). It crystallizes in plates or prisms from alcohol, melts at  $169^\circ$ , and boils at  $264^\circ$ . It does not dissolve in sulphuric acid, as it is incapable of forming a sulpho-acid. Potassium permanganate oxidizes it to benzene hexacarboxylic acid,  $C_6(CO_2H)_6$  (mellitic acid).

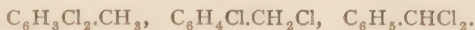
**Dipropyl Benzene**,  $C_6H_4(C_3H_7)_2$  (1, 4), is formed from paradibrom-benzene and propyl iodide, and boils at  $219^\circ$ . When oxidized with dilute nitric acid it affords parapropyl benzoic acid,  $C_6H_4(C_3H_7).CO_2H$  (normal cumic acid). **Propyl-isopropyl Benzene**,  $C_6H_4(C_3H_7)C_3H_7$ , derived from cumyl chloride,  $C_6H_4 \begin{smallmatrix} \diagup CH_2Cl \\ \diagdown CH(CH_3)_2 \end{smallmatrix}$ , and zinc ethyl, boils at  $212^\circ$ , and also yields parapropyl benzoic acid when oxidized with nitric acid.

**Tetraethyl Benzene**,  $C_6H_2(C_2H_5)_4$  (1, 2, 3, 5), is obtained from benzene,  $C_2H_5Br$ , and  $AlCl_3$ , and boils at  $251^\circ$ . It affords phrenitic acid,  $C_6H_2(CO_2H)_4$ , when oxidized with  $MnO_4K$ .

**Hexaethyl Benzene**,  $C_6(C_2H_5)_6 = C_{18}H_{30}$ , crystallizes in large prisms, melting at  $126^\circ$ , and boils at  $292^\circ$  (*Ber.*, 16, 1747).

## HALOGEN DERIVATIVES.

The hydrocarbons of the aromatic series are more readily substituted by chlorine and bromine than the paraffins. In the benzene homologues the substitution occurs both in the residue and in the side groups :—



In the nucleus the halogen atoms are very firmly attached, and are not displaced by the action of  $KOH$ , silver oxide, ammonia, or

sodium sulphite. If nitro-groups enter then the halogens become more reactive. The halogen atoms in the side-chains behave as in the fatty bodies.

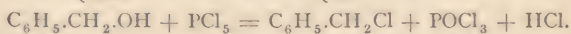
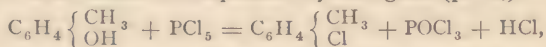
The methods of forming the halogen products are perfectly analogous to those in the fatty-series (p. 64).

(1) Bromine and chlorine manifest an interesting deportment in their substitution. In the cold and in presence of iodine, or  $\text{MoCl}_5$  (also when heated) they act on the nucleus only; from toluene,  $(\text{C}_6\text{H}_5.\text{CH}_3)$ ,  $\text{C}_6\text{H}_4\text{Cl}.\text{CH}_3$ ,  $\text{C}_6\text{H}_4\text{Br}.\text{CH}_3$ , and other products are obtained (*Ber.*, 13, 1216). On the other hand, on conducting chlorine or bromine vapors into boiling toluene (and its homologues) the side-chains are almost exclusively substituted;  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ,  $\text{C}_6\text{H}_5.\text{CHCl}_2$  and  $\text{C}_6\text{H}_5\text{CCl}_3$  are obtained. Acting in the warm and cold alternately (or in presence of iodine), we can substitute hydrogen atoms in the side-chains or in the nucleus (*Beilstein*).

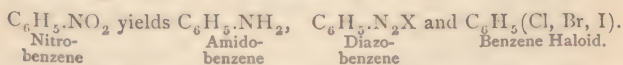
It is only in exceptional cases that iodine acts substitutingly (p. 64).

The action of chlorine and bromine slowly diminishes with the number of halogen atoms already introduced. For further chlorination the substances must be heated with phosphorus chloride, molybdenum chloride, or iodine chloride (*Ber.*, 8, 1296). In such energetic chlorinations the side-chains of the benzene homologues are at last severed. Thus from toluene, xylene, cumene, cymene, etc., we finally obtain perchlorobenzene,  $\text{C}_6\text{Cl}_6$ , while the side groups disappear as  $\text{CCl}_4$ . Naphthalene, anthracene, phenanthrene, and many other benzene compounds behave similarly (*Ber.* 16, 2869). A like decomposition occurs on heating with bromine containing iodine;  $\text{C}_6\text{Br}_6$  and  $\text{CBr}_4$  are formed in this instance. Bromine reacts similarly, but more readily, in the presence of  $\text{Al}_2\text{Br}_6$  (*Ber.*, 16, 2891); from cymene we get  $\text{C}_6\text{Br}_5.\text{CH}_3$  and isopropyl iodide.

(2) Action of the phosphorus haloids upon the phenols and aromatic alcohols (p. 405); here both the hydroxyls in the nucleus and in the side-chains are replaced by halogens (p. 64):—



(3) An important method, and one that is only applicable in the case of benzene derivatives, consists in the transformation of the diazo-compounds (see these). The diazo-group can be replaced by chlorine, bromine and iodine by various reactions. This behavior serves to substitute the halogens for nitro- and amido-groups through the agency of the diazo-compounds:—

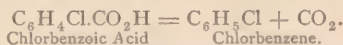


Halogen products can be obtained from substituted amido-compounds by introducing hydrogen for the amido-group through the diazo-derivative:—

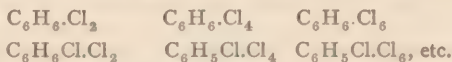




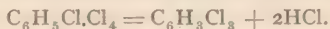
(4) Decomposition of substituted acids by heating them with lime (p. 412) :—



*Addition products* are obtained by letting an excess of chlorine or bromine act upon benzene or the chlor-benzenes, in the sunlight (p. 411) :—



Hexachlorbenzene is also formed by conducting chlorine into boiling benzene; substitution products are produced at the same time. The addition products are solid and do not volatilize without decomposition. When distilled or heated with alkalis, half of the added chlorine (or bromine) breaks off as hydrogen chloride (or bromide) :—



Protracted action of sodium amalgam upon the alcoholic solutions of the halogens brings about the substitution of hydrogen for the halogens. Heating with hydriodic acid and phosphorus effects the same result.

## BENZENE DERIVATIVES.

**Monochlor-benzene**,  $\text{C}_6\text{H}_5\text{Cl}$ , phenyl chloride (the group  $\text{C}_6\text{H}_5$  is called phenyl), is obtained from benzene and from phenol,  $\text{C}_6\text{H}_5.\text{OH}$ , by the action of  $\text{PCl}_5$  upon the latter. It boils at  $132^\circ$  and solidifies at  $-40^\circ$ ; its sp. gr. at  $0^\circ$  is 1.128.

**Dichlor-benzenes**,  $\text{C}_6\text{H}_4\text{Cl}_2$ . In the chlorination of benzene the products are chiefly solid para- and a little liquid ortho- dichlor-benzene.

**Paradichlor-benzene** (1, 4) forms monoclinic needles, melts at  $56^\circ$ , and boils at  $173^\circ$ . It is obtained also by the action of  $\text{PCl}_5$  on para-nitraniline, parachlorphenol and para-phenol-sulphonic acid. It affords a mononitro-product,  $\text{C}_6\text{H}_3\text{Cl}_2.\text{NO}_2$  (1, 4,  $\text{NO}_2$ ), melting at  $55^\circ$ .

**Metadichlor-benzene** (1, 3), from metachlor-aniline,  $\beta$ -dichlor-aniline,  $\text{C}_6\text{H}_3\text{Cl}_2.\text{NH}_2$ , and common dinitro-benzene, is a liquid, and boils at  $172^\circ$ . Its mononitro-derivative melts at  $32^\circ$  (1, 3, 4 —  $\text{NO}_2$  in 4).

**Orthodichlor-benzene** (1, 2), from benzene and orthochlor-phenol, is a liquid, and boils at  $179^\circ$ ; its nitro-derivative melts at  $49^\circ$  (1, 2, 4 —  $\text{NO}_2$  in 4).

**Trichlor-benzenes**,  $\text{C}_6\text{H}_3\text{Cl}_3$ .

Ordinary trichlor-benzene (1, 2, 4) is produced in the chlorination of benzene, or the three dichlor-benzenes, and is also obtained from benzene hexachloride and  $\alpha$ -dichlor-phenol. It melts at  $17^\circ$ , and boils at  $213^\circ$ . Its nitro-compound (1, 2, 4, 5 —  $\text{NO}_2$  in 5) melts at  $58^\circ$ .

*Symmetrical Trichlor-benzene* (1, 3, 5) is obtained from ordinary trichlor-aniline and from  $\text{C}_6\text{H}_5\text{Cl.Cl}_4$ . Long needles, melting at  $63.5^\circ$ , and boiling at  $208^\circ$ .

The *adjacent* trichlor-benzene (1, 2, 3) is formed from trichlor-aniline (1, 2, 3, 4). It consists of plates which dissolve with difficulty in alcohol, melt at  $54^\circ$ , and boil at  $218^\circ$  (*Ann.*, 192, 228).

**Tetrachlor-benzenes,  $C_6H_2Cl_4$ .**

Ordinary (symmetrical) tetrachlor-benzene (1, 2, 4, 5) is produced in the chlorination of benzene, or is obtained from the nitro-derivative of common trichlor-benzene (melting at  $58^\circ$ ). It melts at  $138^\circ$ , and boils at  $243\text{--}246^\circ$ . Boiled with nitric acid it yields chloranil,  $C_6Cl_4O_2$  ( $O_2 = 1, 4$ ). The unsymmetrical tetrachloride (1, 3, 4, 5) = (1, 2, 4, 6) is formed from ordinary trichlor-aniline, and affords needles melting at  $51^\circ$ , and boiling at  $246^\circ$ .

The *adjacent* tetrachlor-benzene (1, 2, 3, 4) is formed from *adjacent* trichlor-aniline (from *metachlor-aniline*), and consists of long needles, melts at  $46^\circ$ , and boils at  $254^\circ$  (*Ann.*, 192, 236).

**Pentachlor-benzene,  $C_6HCl_5$ ,** can only exist in one modification. It is produced by chlorination; forms needles, which melt at  $86^\circ$ , and boil at  $276^\circ$ .

**Hexachlor-benzene,  $C_6Cl_6$ ,** is produced in the chlorination of benzene and other compounds (p. 421) in the presence of  $SbCl_5$  or  $ICl_3$ , and when  $CHCl_3$  or  $C_2Cl_4$  are conducted through tubes heated to redness. It melts at  $226^\circ$ , and boils at  $332^\circ$ .

**Benzene Hexachloride,  $C_6H_6Cl_6$ ,** melts at  $157^\circ$ .

**Monobrom-benzene,  $C_6H_5Br$ ,** from benzene and phenol, boils at  $155^\circ$ ; its specific gravity at  $0^\circ$  is 1.517.

**Dibrom-benzenes,  $C_6H_4Br_2$ .** When bromine acts upon benzene (on heating) (*Ber.*, 10, 1354) it is chiefly the para- and little of the ortho- that results.

*Paradibrom-benzene* (1, 4), from benzene, parabrom-phenol and para-brom-aniline, melts at  $89^\circ$ , and boils at  $218^\circ$ . Its mononitro-derivative (1, 4,  $NO_2$ ) melts at  $85^\circ$ . *Metadibrom-benzene* (1, 3), from ordinary dinitro-benzene and dibrom-aniline, does not solidify at  $-20^\circ$ , and boils at  $219^\circ$ . It yields two mononitro-products, one of which melts at  $61^\circ$  (1, 3, 4 —  $NO_2$  in 4) (chief product), the other, (1, 3, 2 —  $NO_2$  in 2), at  $82.5^\circ$ . *Orthodibrom-benzene* (1, 2), from orthonitraniline and orthonitrobrom benzene, becomes solid below  $0^\circ$ , melts at  $-1^\circ$ , and boils at  $224^\circ$ . Its nitro- product (1, 2, 4 —  $NO_2$  in 4) melts at  $58.6^\circ$ .

**Tribrom-benzenes,  $C_6H_3Br_3$ .** Körner was the first to make a comprehensive investigation of these derivatives with respect to their relations to the three dibrom-benzenes, and to examine into their structure (p. 409).

*Ordinary unsymmetrical* tribrom-benzene (1, 3, 4,) is obtained directly from benzene by the action of bromine. It results from all three dibrom-benzenes, hence (1, 3, 4); also from  $C_6H_6Br_6$ , from common dibrom-phenol and from ordinary dibrom-aniline. It melts at  $44^\circ$ , and boils at  $275^\circ$ . *Symmetrical* tribrom-benzene (1, 3, 5), from tribromaniline, melts at  $119.5^\circ$ , and boils about  $278^\circ$ .

The third *adjacent* tribrom-benzene (1, 2, 3) is formed like the corresponding trichlor-benzene, and melts at  $87^\circ$ .

**Tetrabrombenzenes,  $C_6H_2Br_4$ .** The common variety results from the treatment of benzene and nitro-benzene with bromine. It melts at  $175^\circ$ . The *unsymmetrical* variety (1, 3, 5, Br) is obtained from ordinary tribromaniline and ordinary tribromphenol. It melts at  $97\text{--}99^\circ$  and boils near  $329^\circ$ .

**Pentabrombenzene,  $C_6HBr_5$ ,** the only possible modification, is obtained by acting on benzene with bromine. It melts near  $240^\circ$ .

**Hexabrombenzene,  $C_6Br_6$ ,** is formed by heating benzene (toluene, etc. p. 421) and bromine to  $300\text{--}400^\circ$ ; or by heating  $CBr_4$  to  $300^\circ$ . It consists of needles almost insoluble in alcohol and ether; they melt above  $310^\circ$ .

**Benzene Hexabromide,  $C_6H_6Br_6$ ,** is produced when bromine acts on benzene in sunlight. It is a crystalline compound and decomposes, when heated, into unsymmetrical tribrombenzene and  $HBr$ .

**Iodo-benzene,  $C_6H_5I$ ,** is formed on heating benzene with iodine and iodic

acid to  $200^{\circ}$ ; by the action of phosphorus iodide upon phenol, and from aniline through the diazo compound. It is a colorless liquid, boiling at  $185^{\circ}$ ; its sp. gr. equals 1.69°.

**Di-iodo-benzenes**,  $C_6H_4I_2$ : (1, 4) melts at  $129^{\circ}$  and boils near  $277^{\circ}$ ; (1, 3) melts at  $40.5^{\circ}$  and boils at  $284^{\circ}$ ; both crystallize in leaflets. (1, 2) crystallizes on cooling.

**Tri-iodo-benzene**,  $C_6H_3I_3$  melts at  $76^{\circ}$  and sublimes readily.

**Fluorobenzene**,  $C_6H_5F$ , has been obtained from potassium fluorbenzoate. A liquid with an odor like that of benzene, and boiling at  $85^{\circ}$  (*Ber.*, 17, *Ref.*, 109). **Fluortoluene**,  $C_6H_4F.CH_3$ , obtained in an analogous manner, has an odor like that of bitter-almond oil, and boils at  $114^{\circ}$ .

## DERIVATIVES OF TOLUENE.

**Chlortoluenes**,  $C_6H_4Cl.CH_3$ . Para- and ortho-derivatives are produced in an almost equal amount when toluene is treated with chlorine and bromine (in the cold or in the presence of iodine (p. 421)). The former is a solid and boils somewhat higher than the ortho-compounds. The haloid toluenes may be obtained pure from the amido-toluenes, by replacing the  $NH_2$ -group by halogens; this is accomplished through the diazo-compounds. Thus  $C_6H_4(NH_2).CH_3$  yields  $C_6H_4X.CH_3$ . When heated with a chromic acid mixture (see aromatic acids) the para- and meta-derivatives (by the conversion of the  $CH_3$ -group into  $CO_2H$ ) are oxidized to the corresponding substituted benzoic acids, whereas the ortho-derivatives are attacked with difficulty and completely destroyed. When boiled with dilute nitric acid, with  $MnO_4K$ , or ferricyanide of potassium, all three isomerides (even the ortho) are oxidized to acids.

**Parachlortoluene**,  $C_6H_4Cl.CH_3$  (1, 4), solidifies at  $0^{\circ}$ , melts at  $6.5^{\circ}$  and boils at  $160^{\circ}$ . It yields parachlorbenzoic acid when oxidized with chromic acid or nitric acid. **Orthochlortoluene** (1, 2), from toluene and orthotoluidine, is liquid, and boils at  $156^{\circ}$ ; chromic acid completely decomposes it. **Metachlortoluene** (1, 3) has been prepared from chlorparatoluidine,  $C_6H_3Cl(NH_2).CH_3$ , by replacement of  $NH_2$  by hydrogen. It boils at  $150^{\circ}$  and yields metachlorbenzoic acid.

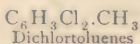
**Benzyl Chloride**,  $C_6H_5.CH_2Cl$ ,  $\alpha$ -chlortoluene, is obtained by the chlorination of boiling toluene (p. 421), and from benzyl alcohol,  $C_6H_5.CH_2.OH$ . It boils at  $176^{\circ}$ . The chlorine atom is readily exchanged. It passes into benzyl alcohol when boiled with water (30 parts). Heated with water and lead nitrate it yields benzaldehyde and by oxidation benzoic acid.

When benzyl chloride is heated to  $200^{\circ}$  with water, the chloride,  $C_{14}H_{13}Cl$ , is produced, and by the distillation of this product, benzyl toluene,  $C_6H_5.CH_2.C_6H_4.CH_3$ , anthracene,  $C_{14}H_{10}$ , and other bodies are formed.

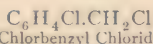
In the nitration of  $C_6H_5.CH_2Cl$ ,  $C_6H_5.CHCl_2$  and  $C_6H_5.CCl_3$ , the products are predominantly *para*-nitro-derivatives with some of the ortho. Further oxidation transforms these into nitro-benzoic acids (*Ber.*, 17, 385 and 1074).

From  $C_6H_5.CHO$ ,  $C_6H_5.CO.CH_3$ ,  $C_6H_5.CO_2H$  and  $C_6H_5.CN$ , we obtain meta-products principally.

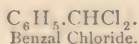
**Dichlortoluenes,  $C_7H_6Cl_2$  :—**



Dichlortoluenes



Chlorbenzyl Chloride

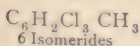


Benzal Chloride.

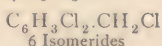
The first compound must have six modifications; the six corresponding dibromtoluenes have all been prepared. There must be three isomerides of the second, and of the third compound only one modification is possible.

**Benzal Chloride,  $C_6H_5.CHCl_2$**  (Benzylene chloride, Chlorobenzene), is formed in the chlorination of boiling toluene and from oil of bitter-almonds,  $C_6H_5.CHO$ , by means of  $PCl_5$ . It is a liquid, boiling at  $206^\circ$ , and has a sp. gr. 1.295 at  $16^\circ$ . It changes to oil of bitter-almonds when exposed to a temperature of  $120^\circ$  in the presence of water.

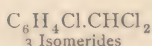
**Trichlortoluenes,  $C_7H_5Cl_3$  :—**



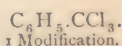
6 Isomerides



6 Isomerides



3 Isomerides



1 Modification.

*Trichlortoluene*,  $C_6H_2Cl_3.CH_3$ , obtained by chlorination, melts at  $75^\circ$  and boils at  $235^\circ$ . *Benzotrichloride*,  $C_6H_5.CCl_3$ , prepared from benzoyl chloride,  $C_6H_5.COCl$ , by action of  $PCl_5$ , is a liquid, and boils at  $213^\circ$ . It yields benzoic acid when heated to  $100^\circ$  with water.

**Pentachlortoluene,  $C_6Cl_5.CH_3$** , melts at  $218^\circ$  and boils at  $301^\circ$ . Further chlorination leads to the substitution of the methyl group, which finally is broken off and hexachlorbenzene,  $C_6Cl_6$  (p. 421), formed.

**Monobromtoluenes,  $C_6H_4Br.CH_3$ .**

*Parabromtoluene* (1, 4), from toluene and paratoluidine, melts at  $28.5^\circ$  and boils at  $185^\circ$ ; it yields parabrombenzoic acid.

**Metabromtoluene** (1, 3) is formed by acting on acetparatoluidine,  $C_6H_4 \left\{ \begin{array}{l} CH_3 \\ NH.C_2H_3O \end{array} \right\}$ , with bromine, and replacing the amido-group by hydrogen; and in a similar manner from acetorthotoluidine. It boils at  $184^\circ$ , and yields metabrombenzoic acid. *Orthobromtoluene* (1, 2), obtained with the para- on treating toluene with bromine, and also from ortho-toluidine, boils at  $182-183^\circ$ ; its sp. gr. at  $20^\circ$  is 1.40. A chromic acid mixture gradually destroys it; dilute nitric acid oxidizes it to orthobrombenzoic acid.

**Benzyl Bromide,  $C_6H_5.CH_2Br$** , is prepared by the action of bromine upon boiling toluene, and by the action of  $HBr$  upon benzyl alcohol. It is a liquid, which provokes tears and boils at  $201^\circ$ ; its specific gravity = 1.438 at  $22^\circ$ .

**Dibromtoluenes,  $C_6H_3Br_2.CH_3$** . The six possible isomerides have been prepared in various ways (*Ber.*, 13, 970).

**Benzal Bromide,  $C_6H_5.CHBr_2$** , from benzaldehyde, decomposes upon distillation.

**Ortho-Brombenzyl Bromide,  $C_6H_4Br.CH_2Br$** , from ortho-bromtoluene, melts at  $30^\circ$ , and with sodium forms anthracene and phenanthrene. Chromic acid does not oxidize it.

**Iodo-toluenes,  $C_6H_4I.CH_3$ .**

*Paraiodotoluene* (1, 4), from paratoluidine, crystallizes in shining laminae, melts at  $35^\circ$  and boils at  $211^\circ$ . Chromic acid converts it into paraiodobenzoic acid.

*Metaiodotoluene* (1, 3), from liquid metatoluidine, is a liquid boiling at  $207^\circ$ , and when oxidized by chromic acid yields metaiodobenzoic acid. *Orthoiodo-*



*toluene* (1, 2), from orthotoluidine, is liquid, and boils at  $205^{\circ}$ . When oxidized with dilute nitric acid it becomes orthoiodobenzoic acid.

**Benzyl Iodide**,  $C_6H_5.CH_2I$ , is obtained from benzyl chloride by the action of  $HI$  or  $KI$ . It melts at  $24^{\circ}$  and decomposes when distilled.

The halogen substitution products of the higher benzenes are in part mentioned with the latter; for those of ethyl benzene see p. 416.

## NITRO-DERIVATIVES.

All benzene derivatives readily pass into nitro-products (p. 72) through the action of nitric acid, the benzene nucleus (not the side-chains) being substituted:—



The substance to be nitrated is gradually added to concentrated or fuming nitric acid, when it will dissolve with evolution of brown vapors. When this does not occur heat should be applied. On pouring the solution into water the nitro-products, not soluble in water, are precipitated. A mixture of nitric acid (1 part) and sulphuric acid (2 parts) acts more energetically, as the second acid combines with any water that may be formed in the reaction. The nitration is considerably moderated by previously dissolving the substance in glacial acetic acid. The more alkyl groups there are in a benzene hydrocarbon, the more readily will it be nitrated.

Nitro-derivatives of substituted hydrocarbons are obtained: (1) by nitration of the halogen derivatives, while in the inverse action of chlorine and bromine upon nitro-derivatives in the heat the nitro-group is generally eliminated; (2) by the action of  $PCl_5$  and  $PBr_5$  upon nitro-phenols, *e. g.*,  $C_6H_4(NO_2).OH$ , when the hydroxyl group is replaced by halogens; (3) from nitro-amido-compounds, the amido-group being exchanged for halogens through the agency of the diazo-compounds; (4) by decomposition of nitro-acids when heated with lime (p. 412).

Various reducing agents convert the nitro into amido-compounds (p. 430). Sodium amalgam or alcoholic potash produces azo-compounds. The nitro-derivatives generally possess a faint yellow color; ammonia deepens the latter. The mono-nitro-benzenes usually boil undecomposed; the di-derivatives are not volatile.

## DERIVATIVES OF BENZENE.

**Nitro-benzene**,  $C_6H_5.NO_2$ , is obtained by dissolving benzene in a mixture of common nitric and sulphuric acids. It is a bright yellow liquid, possessing an odor resembling that of oil of bitter almonds (artificial almond oil, oil of mirbane), and a specific gravity at  $0^{\circ}$  of 1.20. It becomes crystalline at  $+3^{\circ}$  and boils at  $205^{\circ}$ .

**Dinitro-benzenes**,  $C_6H_4(NO_2)_2$ . The three dinitro-benzenes are produced, if in the nitration with fuming nitric acid, the mix-

ture be boiled a short time. On crystallizing from alcohol the meta-compound, formed in greatest quantity, separates first, whereas the ortho- and para- dinitro-derivatives remain in solution (*Ber.*, 7, 1372). For the production of the ortho-dinitro-benzene, see *Ber.*, 17, Ref. 20.

The ortho-compound (like other ortho-dinitro-benzenes) exchanges an  $\text{NO}_2$  group for OH when boiled with caustic soda, forming ortho-nitro-phenol,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{OH}$ . Likewise on heating ortho-dinitro-compounds with alcoholic ammonia (and with anilines) we have ortho-nitranilines, *e. g.*,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{NH}_2$ , produced. Ferricyanide of potash and caustic soda oxidize the metadinitro-benzenes to dinitrophenols; they unite with aniline, yielding molecular compounds. Meta- and para-dinitrobenzenes combine, too, with benzenes, naphthalenes, etc. (*Ber.*, 16, 234).

*Meta-dinitrobenzene* (1, 3) is obtained from common dinitrotoluene (1, 2, 4,  $\text{CH}_3$  in 1), and from  $\alpha$ - and  $\beta$ -dinitraniline; it was formerly called para. It crystallizes in long, colorless needles, difficultly soluble in cold alcohol and melting at  $89.9^\circ$ . By reduction it yields (1, 3)-nitraniline and (1, 3)-phenylene diamine (melting at  $63^\circ$ ). When heated with potassium ferricyanide and caustic soda it forms  $\alpha$ - and  $\beta$ -dinitrophenol,  $\text{C}_6\text{H}_3(\text{NO}_2)_2.\text{OH}$ . Metadinitro-benzene heated with alcoholic potash has one of its nitro-groups removed with formation of  $\text{C}_6\text{H}_2(\text{NO}_2)(\text{O.C}_2\text{H}_5).\text{CN}$ , which, heated with alcoholic potash, yields dioxyethyl benzonitrile,  $\text{C}_6\text{H}_3(\text{O.C}_2\text{H}_5)_2\text{CN}$ . This fused with KOH affords dioxybenzoic acid. When paradinitrobenzene (not ortho) is boiled with alcoholic potassium cyanide potassium nitrite is also formed (*Ber.*, 17, Ref. 19).

*Paradinitrobenzene* (1, 4) forms colorless needles, is more difficultly soluble in alcohol, melts at  $173^\circ$  and yields (1, 4)-nitraniline and (1, 4)-phenylene diamine (melting at  $140^\circ$ ).

*Orthodinitrobenzene* (1, 2) formed in very small amount in nitration, crystallizes in plates from hot water and melts at  $118^\circ$ . It yields (1, 2)-nitraniline, and (1, 2)-phenylene diamine (melting at  $99^\circ$ ).

**Symmetrical Trinitrobenzene**,  $\text{C}_6\text{H}_3(\text{NO}_2)_3$  (1, 3, 5), is produced by heating meta-dinitrobenzene with  $\text{HNO}_3$  and pyrosulphuric acid to  $140^\circ$ ; it crystallizes in white laminae or needles and melts at  $121$ – $122^\circ$ . It becomes trinitrophenol (Picric Acid) when heated with ferricyanide of potassium and caustic soda. It unites with benzenes and anilines, forming molecular compounds (*Ber.*, 13, 2346). Para-dinitrobenzene affords **unsymmetrical trinitrobenzene** (1, 2, 4) (*Ber.*, 17, Ref. 233).

#### Nitro-haloid Benzenes, $\text{C}_6\text{H}_4\text{X}(\text{NO}_2)$ .

Upon nitrating chlor-, brom-, and iodo-benzene, para- and ortho-mononitro products result; the first in larger quantity (p. 424). The meta-derivatives are prepared from meta-nitraniline,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{NH}_2$  (from common dinitro-benzene), by replacement of the amido group by halogens, effected by means of the diazo-compounds. The para- and ortho- compounds can be similarly prepared from the corresponding nitranilines.  $\text{PCl}_5$  also converts nitro-phenols,  $\text{C}_6\text{H}_4(\text{NO}_2).\text{OH}$ , into chlornitro-derivatives. Metachlornitro-benzene is obtained by the chlorination of nitrobenzene in the presence of iodine, or  $\text{SbCl}_3$ .

The isomeric mononitro-chlor-, brom-, and iodo-benzenes have the following melting points:—

	(1, 2)	(1, 3)	(1, 4)
$\text{C}_6\text{H}_4\text{Cl}(\text{NO}_2)$	$32.5^\circ$	$44.4^\circ$	$83^\circ$
$\text{C}_6\text{H}_4\text{Br}(\text{NO}_2)$	$41.5^\circ$	$56^\circ$	$126^\circ$
$\text{C}_6\text{H}_4\text{I}(\text{NO}_2)$	$49^\circ$	$33^\circ$	$171^\circ$

Meta-chlornitrobenzene occurs in two physical modifications: if rapidly cooled

after fusion, it melts at  $23.7^{\circ}$ , but in a short time it reverts to the stable modification, melting at  $44.4^{\circ}$ .

As may be seen above, the para-derivatives possess the highest melting points, and the meta- are generally higher than the ortho. A similar deportment is manifested by almost all di-derivatives of benzene (p. 434). Again, the para-compounds are usually more difficultly soluble in alcohol. The different behavior of chlor- and brom-nitrobenzenes with caustic potash and ammonia is very instructive. The ortho- and para-derivatives (latter with more difficulty than the former) afford the corresponding nitro-phenols,  $C_6H_4(NO_2).OH$ , when heated with aqueous or alcoholic potash in closed tubes to  $120^{\circ}$ . In this reaction the halogens are replaced by hydroxyl. The meta-derivatives do not react under the above conditions. The ortho- and para-compounds also yield corresponding nitranilines,  $C_6H_4(NO_2).NH_2$ , when heated to  $100^{\circ}$  with alcoholic ammonia, while the (1, 3)-chlor- and brom-nitrobenzenes do not react (compare dinitrobenzenes (p. 427) and the nitranilines).

In the nitration of the mono-haloid benzenes, as well as in the chlorination (bromination) of benzene (p. 422) and toluene (p. 424), the para- and ortho-compounds are almost the only products. In the further nitration (chlorination) we get only tri-substitution products of the structure (1,2,4—the entering groups occupy 2,4); the nitro-groups and halogens take the meta-position (2,4) = (1,3). So in the nitration (chlorination) of phenol,  $C_6H_5.OH$ , of toluene,  $C_6H_5.CH_3$ , and of aniline,  $C_6H_5.NH_2$ , the first derivatives are only of the ortho- and para-varieties, and finally di-substitution products of the structure (1,2,4—the groups  $OH$ ,  $CH_3$ ,  $NH_2$  occupy 1). Hence, *in the tri-derivatives the tendency is to form the unsymmetrical combination* (1,2,4), (*Ann.*, 192, 219). In the *di-derivatives* the usual products are para- and ortho-compounds, and it is only in the nitration (chlorination) of nitrobenzene,  $C_6H_5(NO_2)$ , benzoic acid,  $C_6H_5.CO_2H$ , benzaldehyde,  $C_6H_5.CHO$ , benzonitrile,  $C_6H_5.CN$ , and some additional compounds (with acid side-chains), that the *meta-derivatives predominate* in the presence of the ortho- and para-varieties (p. 434). And thus, too, in the treatment of benzene with sulphuric acid, the meta-disulpho-acid,  $C_6H_4(SO_3H)_2$ , is the chief product.

If an unsymmetrical tri-derivate (1,2,4) be further substituted, unsymmetrical tetra-derivatives (1,2,4,6) are generally produced. Thus, from aniline,  $C_6H_5.NH_2$ , phenol,  $C_6H_5.OH$ , etc., we obtain compounds like  $C_6H_2Cl_3.NH_2$  and  $C_6H_2(NO_2)_3.OH$  (1,2,4,6— $NH_2$  or  $OH$  in 1), in which the entering groups occupy the meta-position (2,4,6 = 1,3,5) with reference to each other. By the elimination of the  $OH$  and  $NH_2$  groups in them, we obtain symmetrical tri-derivatives,  $C_6H_3X_3$  (1,3,5).

**$\alpha$ -Dinitro-chlorbenzene**,  $C_6H_3Cl(NO_2)_2$  (1, 2, 4), is obtained from (1, 2)- and (1, 4) chloronitro-benzene, or from ordinary dinitrophenol, and by the direct nitration of  $C_6H_5Cl$ . It melts at  $53.4^\circ$ . The nitro-groups in it hold the position (1, 3) = (2, 4).

**$\alpha$ -Dinitro-brombenzene**,  $C_6H_3Br(NO_2)_2$  (1, 2, 4), is formed like the preceding and melts at  $75.3^\circ$ . When boiled with a soda-solution both yield ordinary dinitrophenol, and with alcoholic ammonia  $\alpha$ -dinitraniline (melting at  $182^\circ$ ).

The nitration of meta-chlor and bromnitro-benzene affords the isomerides  **$\beta$ -chlor- and bromdinitro-benzenes**,  $C_6H_3Cl(NO_2)_2$ , and  $C_6H_3Br(NO_2)_2$  (1, 3, 4). Cl and Br occupy 1); the first exists in three modifications, which melt at  $36.3^\circ$ ,  $37^\circ$ , and  $38.8^\circ$  (*Ber.*, 9, 760); the second consists of yellow plates, melting at  $59.4^\circ$ .

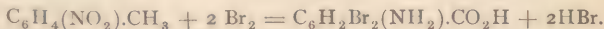
**Trinitro-chlorbenzene**,  $C_6H_3Cl(NO_2)_3$  (1, 3, 5, Cl), **Picryl Chloride**, is obtained from picric acid by the action of  $PCl_5$ . It melts at  $83^\circ$ . It is converted into picramide,  $C_6H_2(NH_2)(NO_2)_3$ , with ammonia, and into picric acid when boiled with water.

#### DERIVATIVES OF TOLUENE.

By nitration toluene affords chiefly two isomeric **nitro-toluenes**,  $C_6H_4(NO_2).CH_3$ , the solid para-compound and the liquid ortho-derivative. They can be separated by fractional distillation. The para-nitrotoluene predominates when the nitration occurs at an elevated temperature and fuming acid is employed, but at low temperatures, and with nitric and sulphuric acids, the ortho-body is in greater quantity (about 66 per cent).

**Paranitro-toluene** (1, 4) forms large prisms; melts at  $54^\circ$  and boils at  $237^\circ$ . Chromic acid oxidizes it to paranitro-benzoic acid; paratoluidine is the product of its reduction. Chlorination at  $150^\circ$  produces paranitro-benzal chloride,  $C_6H_4(NO_2).CHCl_2$ , which forms paranitro-benzaldehyde with  $SO_4H_2$ .

**Orthonitro-toluene** (1, 2) is liquid, and boils at  $223^\circ$ ; its specific gravity at  $23^\circ$  is 1.163. It is also formed in the partial reduction of dinitro-toluene with ammonium sulphide, and the replacement of the  $NH_2$  group of the resulting amide by hydrogen. Chromic acid destroys it, but when oxidized with  $HNO_3$ ,  $MnO_4K$ , or potassium ferricyanide, orthonitro-benzoic acid is the product; it yields orthotoluidine by reduction. Bromine added to orthonitro-toluene at  $170^\circ$  produces dibromanthranilic acid:—



**Metanitro-toluene** (1, 3) is formed if acetparatoluidine,  $C_6H_4 \begin{Bmatrix} CH_3 \\ NH.C_2H_5O \end{Bmatrix}$ , is nitrated, and the amido-group replaced by hydrogen. It melts at  $16^\circ$  and boils at  $230^\circ$ . When oxidized, it yields metanitro-benzoic acid; when reduced, metatoluidine.

Ordinary  **$\alpha$ -Dinitro-toluene**,  $C_6H_3(NO_2)_2.CH_3$  (1, 2, 4— $CH_3$  occupying 1), is obtained from toluene, and from (1, 4)- and (1, 2)-nitrotoluene on boiling with fuming nitric acid. It crystallizes in long needles, melts at  $71^\circ$  and boils near  $300^\circ$ . It can be oxidized to dinitro-benzoic acid, from which we obtain (1, 3)-dinitro-benzene. Ammonium sulphide reduces the  $NO_2$  group (in 4), and affords amido-nitrotoluene. Symmetrical **dinitrotoluene** (1, 3, 5) is formed from dinitro-paratoluidine, and melts at  $92^\circ$ .

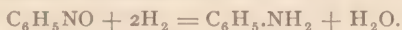


**Trinitro-toluene**,  $C_6H_2(NO_2)_3.CH_3$  (1, 2, 4, 6— $CH_3$  occupying 1), is prepared by heating toluene with nitric and sulphuric acids. It melts at  $82^\circ$ , and is oxidized with difficulty. It forms molecular compounds with benzenes, and anilines (p. 427), and yields symmetrical trinitrobenzene when heated with nitric acid.

## NITROSO-COMPOUNDS.

Nitroso-benzene and nitroso-naphthalene are the only known derivatives in which the nitroso-group occupies the position of benzene hydrogen. The so-called nitroso-phenols (see these), according to latest researches, possess a very different constitution, although they afford the nitroso-reaction (p. 79).

**Nitroso-benzene**,  $C_6H_5.NO$ , is produced by the action of  $NOCl$  or  $NOBr$  upon a solution of mercury diphenyl,  $(C_6H_5)_2Hg$ , in benzene or carbon disulphide, or by letting nitrous acid act upon diphenyl tin chloride,  $(C_6H_5)_2SnCl_2$ . It is only known in solution, and has a sharp odor and green color. Tin and hydrochloric acid reduce it to aniline:—



When warmed with aniline acetate azobenzene is formed:—



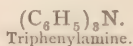
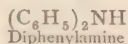
The *isonitroso-compounds*, containing the group  $=N.OH$ , are described in connection with the substances from which they are obtained.

## AMIDO-COMPOUNDS.

These arise in the substitution of amido-groups for the hydrogen of benzene:—



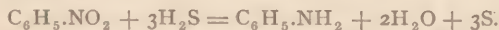
Or, they may be considered as ammonia derivatives, from which might be concluded the existence of primary, secondary and tertiary amines of the benzene series (p. 123):—



The true analogues, *e. g.*,  $C_6H_5.CH_2.NH_2$ , of amines of the fatty series are obtained when the hydrogen of the side-chains is replaced by the amido-group. They are considered later.

The amido-compounds of the benzene series are prepared almost exclusively by the reduction of nitro-derivatives. The most important methods of reduction are:—

(1) The action of ammonium sulphide in alcoholic solution (Zinin in 1842):—

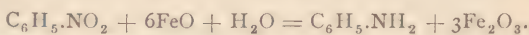


The nitro-compound is dissolved in alcohol, concentrated ammonia added and  $H_2S$ , while warming, conducted into the mixture as long as sulphur is precipi-

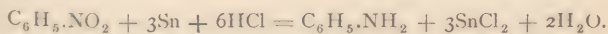
tated. Then filter and concentrate the filtrate. In using this reaction with the di- and tri-nitro-compounds only one nitro-group is reduced at first, and in this manner it is therefore easy to obtain intermediate products, like the nitroamido-compounds. It is only by continued heating that the second nitro-group is reduced.

In the case of chlor-nitro-benzenes the nitro-group is only reduced by ammonium sulphide when it is not *adjacent* to the chlorine or another nitro-group; in the reverse instance sulphur will replace the chlorine or a nitro-group (*Ber.*, **11**, 2056 and **1156**).

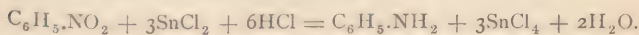
(2) Action of zinc and hydrochloric acid upon the alcoholic solution of nitro-compounds (Hofmann); or iron filings and acetic or hydrochloric acid (Béchamp). The latter is applied technically in the manufacture of aniline or toluidine; the reduction is accomplished by the nascent hydrogen and the resulting ferrous oxide:—



(3) Action of tin and hydrochloric acid (or acetic acid) (Roussin):—



Stannous chloride reacts similarly:—



This method serves also for the quantitative determination of the nitro-groups (*Ber.*, **11**, 35 and 40).

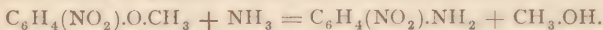
Pour fuming hydrochloric acid over the nitro-compound and gradually add the calculated quantity of granulated tin ( $1\frac{1}{2}$  Sn for  $\text{1NO}_2$ ); after a little time, usually without heating, a violent reaction ensues, and the tin and nitro-derivative both dissolve. The solution contains the double salts, *e. g.*,  $(\text{C}_6\text{H}_5\cdot\text{NH}_2\cdot\text{HCl})_2\text{SnCl}_4$ , formed by the HCl-salt of the amide combining with tin chloride. These salts generally crystallize well. The tin is precipitated from the hot solution by  $\text{H}_2\text{S}$ , the sulphide is filtered off and the filtrate contains the hydrochloride salt of the amido-compound. Alkalies will set the latter free. Sometimes in using tin and hydrochloric acid chlorinated amido-compounds are produced, therefore, in such cases it is advisable to substitute acetic acid.

In this procedure, which is principally employed in laboratories, all the nitro-groups present in a compound are simultaneously reduced. The reduction can, though, be limited to single groups (Kekulé), if we apply an alcoholic HCl solution and take only half the tin requisite for complete reduction; thus, nitraniline results from dinitrobenzene.

Other reducing agents, finding occasional application, are: sodium arsenite, zinc dust (in alcoholic or ammoniacal solutions), tin and acetic acid (*Ber.*, **15**, 2105), and HI and phosphorus iodide. Sodium amalgam, on the other hand, reduces nitro- to azo-compounds. A procedure, very well adapted for unsaturated nitro-compounds, consists in the use of ferrous sulphate and baryta-water or ammonia (*Ber.*, **15**, 2299).

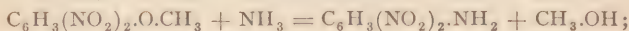
Only traces of amido-derivatives can be had by heating the haloid compounds, *e. g.*,  $C_6H_5Br$ , with ammonia: the same may be remarked of the phenols. Both classes of compounds, however, react more readily providing nitro-groups exist in the benzene nucleus. Thus, when (1, 2)- and (1, 4)- chlor- and brom-nitrobenzenes are heated with alcoholic ammonia, the corresponding nitranilines are produced, whereas the meta-compounds do not react (p. 428).

Amido-derivatives are similarly formed from the nitranisoles (alkylized phenols), when heated with aqueous or alcoholic ammonia to  $180-200^\circ$ :—



Here again it is the para- and ortho-compounds which react, not the meta-variety.

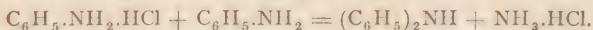
The halogen atoms and oxyalkyls are more reactive in the presence of two or three nitro-groups. Thus  $\alpha$ -chlor- and brom-dinitrobenzene yield dinitraniline (p. 429); dinitroanilines are formed from the  $\alpha$ - and  $\beta$  dinitrophenols (their ethers) (*Ann.*, 174, 276):—



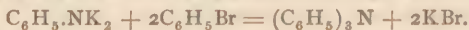
and from dinitroanisic acid is obtained chrysanic acid.

In a few ortho-dinitro-compounds ammonia (also aniline) can replace a nitro-group by  $NH_2$ , thus ortho-dinitrobenzene yields ortho-nitraniline,  $\beta$ -dinitrochlorbenzene yields nitroamido-chlorbenzene (p. 426). They can also be directly transformed into amido-benzenes by heating them to  $300^\circ$  with ammonia-zinc chloride ( $ZnCl_2.NH_3$ ), or ammonia-calcium chloride:  $C_6H_5.OH + NH_3 = C_6H_5.NH_2 + H_2O$  (*Ber.*, 16, 8). The naphthols react even more readily. The divalent phenols react in like manner with aniline (*Ber.*, 16, 2812).

The *secondary* and *tertiary* phenylamines cannot be prepared from the primary, *e. g.*,  $C_6H_5.NH_2$ , by action of  $C_6H_5Cl$  or  $C_6H_5Br$ . The secondary are obtained by heating the anilines with HCl-anilines (like the secondary acid amides) (p. 207):—



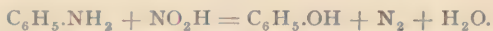
The tertiary phenylamines are prepared by treating the potassium compounds,  $C_6H_5.NK_2$  or  $(C_6H_5)_2NK$ , with  $C_6H_5Br$ :—



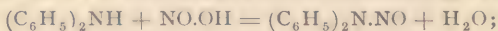
The amido-derivatives of the benzene hydrocarbons are organic bases; they combine with acids to form salts, just as the amines do, and are freed again by alkalis. But they are far more feeble bases than the alkylamines, because the phenyl group possesses a more negative character (p. 404). The secondary phenylamines, *e. g.*,  $(C_6H_5)_2NH$ , are even less basic; their salts are decomposed by water, and tertiary triphenylamine is not capable of producing salts.

When negative groups enter the primary phenylamines they further diminish their basic character; the salts of substituted anilines, like  $C_6H_3Cl_2.NH_2$  and  $C_6H_3(NO_2)_2.NH_2$ , are decomposed by water or incapable of existence.

The behavior of the phenylamines towards nitrous acid is very characteristic; it is perfectly analogous to that of the alkylamines (p. 125). The primary phenylamines exchange the group  $\text{NH}_2$  for  $\text{OH}$ , and form phenols:—



Diazo-compounds and diazoamido-derivatives (see these) are intermediate products. The secondary phenylamines, *e. g.*,  $(\text{C}_6\text{H}_5)_2\text{NH}$  and  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CH}_3$ , yield nitrosamines (p. 128):—

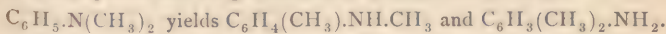


while from tertiary amido-derivatives we get the nitroso-products of the benzene nucleus:—

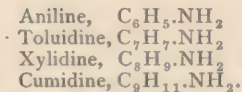


The primary phenylamines only are adapted to the formation of carbylamines and mustard oils (pp. 240 and 246). Furfurol combines with all the amido-benzene derivatives, forming intense red-colored compounds.

On heating the  $\text{HCl}$ -salts of methyl and dimethyl aniline to  $300^\circ$ , the methyl group is transposed, and we get toluidene, xylidene, etc. (p. 412).



A similar alkylizing of the benzene nucleus occurs on heating the  $\text{HCl}$ -anilines with alcohols to  $300^\circ$ , or the anilines with alcohols and  $\text{ZnCl}_2$  to  $280^\circ$  (*Ber.*, 16, 105).



**Aniline**,  $\text{C}_6\text{H}_5\cdot\text{NH}_2$ , amidobenzene, was first noticed by Unverdorben in 1826, in the dry distillation of indigo (crystallin), and later by Fritsche in the distillation of indigo with caustic potash (*Anilin*, 1841). Runge discovered (1834) it in coal-tar, and called it *cyanole*. Zinin was the first to prepare it artificially (1841), by reducing nitrobenzene with ammonium sulphide. It is formed in the dry distillation of many nitrogenous substances, for example, bituminous coal, bones, indigo and isatine. At present it is exclusively made by reducing nitrobenzene.

In the preparation of aniline on a large scale, nitrobenzene is heated with iron filings and hydrochloric acid (p. 431). The product of the reaction is mixed with lime and distilled with superheated steam. In a small way the reduction is best executed with tin and hydrochloric acid.

Aniline is a colorless liquid with a faint, peculiar odor, and boils at  $183^\circ$  (corr.); its specific gravity at  $0^\circ$  is 1.036. When perfectly pure it solidifies on cooling, and melts at  $-8^\circ$ . It is difficultly sol-



uble in water (1 part in 31 parts at  $12^{\circ}$ ), but dissolves readily in alcohol and ether. It shows a neutral reaction with litmus. When heated it expels ammonia from its salts, while in the cold ammonia separates it from its salts. Exposed to air aniline gradually assumes a brown color, and resinifies. Bleaching lime imparts a purple color to the solution. When a pine shaving is moistened with aniline salts it becomes yellow in color. On adding sulphuric acid and a few drops of potassium chromate to aniline, a red color appears; later it becomes an intense blue.

As a base aniline unites directly with acids, and also with some salts— $(C_6H_5N)_2$ ,  $SnCl_2$ ,  $(C_6H_7N)_2.CuSO_4$ . Its salts crystallize well, and dissolve readily in water. The  $HCl$ -salt,  $C_6H_7N.HCl$ , forms deliquescent needles; platinic chloride precipitates a yellow-colored double salt,  $(C_6H_7N.HCl)_2.PtCl_4$ , from the alcoholic solution. The *nitrate*,  $C_6H_7N.NO_3H$ , crystallizes in large rhombic plates; the *oxalate*,  $(C_6H_7N)_2.C_2O_4H_2$ , obtained by mixing the alcoholic solutions, forms rhombic prisms.

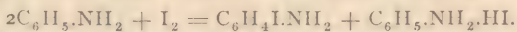
On warming aniline with potassium, the hydrogen of the amido-group is replaced with formation of the compounds  $C_6H_5.NHK$  and  $C_6H_5.NK_2$ ; sodium does not react until heated to  $200^{\circ}$ . It acts more readily providing one hydrogen atom of the amido-group is substituted by acid radicals (as in acetaniline  $C_6H_5.NH.C_2H_3O$ ), or if halogen atoms be present in the benzene nucleus; in this case the halogen is reduced by the nascent hydrogen. The sodium compounds are oxidized to azo-compounds, when they are exposed to the air.

### ANILINE SUBSTITUTION PRODUCTS.

These are obtained: (1) By the direct substitution of aniline. The anilines, like the phenols, are more susceptible of substitution than the benzenes. The action of the halogens is so energetic that the reaction requires to be moderated. When chlorine or bromine water acts upon the aqueous solution of aniline salts, their hydrogen atoms are directly substituted. Nitric acid converts aniline into nitrophenols. To get the mono- and di-substitution products, it is necessary to employ as points of departure the acid anilides, *e. g.*, acetanilide,  $C_6H_5.NH.C_2H_3O$ ; these are first substituted, and the substituted anilines separated from them by boiling with alkalis or hydrochloric acid, or with sulphuric acid.

On allowing chlorine and bromine (in aqueous solution, or in vapor form) to act upon acetanilide suspended in water, only para-compounds are produced (p. 428), because the ortho-derivatives formed at the same time immediately pass into dihalogen derivatives. In the nitration of acetanilide mono-derivatives of the para-, ortho- and meta-series are formed. By nitration in presence of much sulphuric acid, meta-nitro-derivatives predominate (p. 436). Consult p. 428 and *Ber.*, 13, 962, for further information upon the influence exerted by the amido-group upon the position taken by bromine and  $NO_2$  in substitutions. When ortho- and para-substituted anilines are chlorinated, they almost invariably furnish trisubstituted products (1, 2, 4, 6), whereas the meta-series yield tetra- and penta-substitution products (*Ber.*, 15, 1328).

Iodine is capable of directly substituting the anilines, as the resulting hydriodic acid is taken up by excess of aniline:—



(2) By the reduction of halogen nitrobenzenes by means of tin and hydrochloric acid, or ammonium sulphide (p. 430); thus, the three  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$  yield the corresponding  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ .

(3) The nitranilines can be prepared by heating haloid nitrobenzenes to  $150\text{--}180^\circ$  with alcoholic ammonia; or by heating the ethers of the nitrophenols, *e. g.*,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , with aqueous ammonia. In both instances the para- and ortho-compounds, and not the meta-, react (p. 428).

(4) The halogen anilines can be obtained from the nitro-anilines by first replacing the amido-group by halogens. This is accomplished through the diazo-compounds. The next step is, then, to reduce the nitro-group:—



The ortho-compounds are more feeble bases than the para and meta.

**Ortho- and Meta-Chloraniline**, from the corresponding chlornitro-benzenes, are liquids; the first boils at  $207^\circ$ ; its specific gravity at  $0^\circ$  is 1.23; the second boils at  $230^\circ$ ; its specific gravity at  $0^\circ$  is 1.24. **Parachloraniline**, formed from (1, 4)-nitraniline and nitrochlorbenzene, and by the chlorination of acetanilide, crystallizes in shining, rhombic octahedra, which are somewhat soluble in hot water. It melts at  $70\text{--}71^\circ$  and boils at  $230\text{--}231^\circ$ , with scarcely any decomposition. The HCl-salt is rather difficultly soluble in cold water.

**Ortho-bromaniline**,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ , from o-(Br.NO<sub>2</sub>) and o-(NH<sub>2</sub>.NO<sub>2</sub>), crystallizes in needles, melting at  $31.5^\circ$  and boiling at  $229^\circ$ . **Metabromaniline**, from m-nitroaniline and m-bromnitrobenzene, melts at  $18^\circ$  and boils at  $251^\circ$ . **Parabromaniline**, from p-nitraniline and p-nitrobrombenzene, is easily obtained by conducting bromine vapor into acetanilide. It crystallizes in shining, rhombic octahedra, and melts at  $63^\circ$  ( $66^\circ$ ). The action of sodium upon the ethereal solution produces benzenide. When distilled it breaks up into aniline,  $\alpha$ -dibromaniline and  $\alpha$ -tribromaniline.

**Ortho-iodoaniline**,  $\text{C}_6\text{H}_4\text{I}\cdot\text{NH}_2$ , has not been prepared. **Metaiodoaniline**, from m-nitraniline, forms silvery laminae, and melts at  $25^\circ$ . **Paraiodoaniline** is formed from p-nitroiodobenzene and by the direct action of iodine upon aniline, or by the action of chlor-iodine upon acetanilide. It consists of needles or prisms, melting at  $60^\circ$  ( $83^\circ$ ), and somewhat soluble in hot water. With ethyl iodide it yields ethyl-aniline:—



$\alpha$ -**Dichloraniline**,  $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$ , from dichloracetanilide (1, 2, 4—NH<sub>2</sub> in 1), crystallizes in needles, and melts at  $63^\circ$ .  $\beta$ -**Dichloraniline**, from nitro-(1, 4)-dichlorbenzene (p. 422), melts at  $54^\circ$  (*Ann.*, 196, 215).

$\alpha$ -**Dibromaniline**,  $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NH}_2$  (1, 2, 4—NH<sub>2</sub> in 1), is obtained from dibromacetanilide and from nitro-(1, 3)-dibrombenzene (melting at  $61^\circ$ , p. 423); in melts at  $79^\circ$ .  $\beta$ -**Dibromaniline**, from nitro-(1, 4)-dibrombenzene, melts at  $51\text{--}52^\circ$ .

***α*-Trichloraniline**,  $C_6H_2Cl_3.NH_2$  (chlorine in 1, 3, 5), is formed by conducting chlorine into the aqueous solution of *HCl*-aniline. It melts at  $77.5^\circ$  and boils at  $260^\circ$ . It no longer combines with acids. Symmetrical trichlorbenzene is obtained from it by substituting *H* for  $NH_2$ . ***β*-Trichloraniline**, (1, 2, 4, 5 —  $NH_2$  in 1), from nitro-(1, 2, 4)-trichlorbenzene, melts at  $96.5^\circ$  and boils at  $270^\circ$ .

***α*-Tribromaniline**,  $C_6H_2Br_3.NH_2$  (bromine in 1, 3, 5), is formed on conducting bromine vapors into aqueous *HCl*-aniline; it crystallizes in long needles, melts at  $119^\circ$ , and does not yield salts readily. (*Ber.*, 16, 635). It affords symmetrical tribrombenzene. ***β*-Tribromaniline** (1, 2, 4, 5 —  $NH_2$  in 1) is obtained from ordinary tribrombenzene (1, 2, 4) by nitration and reduction, and does not melt, even at  $130^\circ$ .

**Nitranilines**,  $C_6H_4(NO_2).NH_2$ :—

		(1, 2)	(1, 3)	(1, 4).
$C_6H_4 \left\{ \begin{array}{l} NH_2 \\ NO_2 \end{array} \right.$	M. P.	$71^\circ$	$114^\circ$	$147^\circ$
$C_6H_4 \left\{ \begin{array}{l} NH_2 \\ NH_2 \end{array} \right.$	"	$102^\circ$	$63^\circ$	$147^\circ$
$C_6H_4 \left\{ \begin{array}{l} NO_2 \\ NO_2 \end{array} \right.$	"	$118^\circ$	$90^\circ$	$172^\circ$

The three nitranilines can be obtained from the three corresponding dinitrobenzenes, by incomplete reduction with ammonium sulphide (p. 430). Ortho- and para-nitranilines are also produced from the corresponding haloid nitrobenzenes, the ethers of nitrophenols and dinitrobenzenes, upon heating with ammonia (p. 432); also by the nitration of acetaniline. The easiest course to pursue in making the three compounds, is to dissolve aniline-hydrosulphate in an excess of concentrated sulphuric acid, and add the calculated amount of fuming nitric acid. Precipitate with water and distil in a current of steam, when the ortho- and the meta-products pass over, while the para remains. The para and meta occur rather abundantly, the ortho only in meagre amount (*Ber.*, 10, 1716; 17, 261).

**Ortho-nitraniline** (1, 2) forms yellow needles, melting at  $71^\circ$ ; it dissolves in water and alcohol more readily than its isomerides, and is more reactive. It yields (1, 2)-diamido-benzene when reduced.

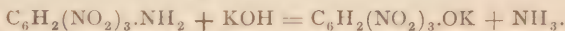
**Metanitraniline** (1, 3) consists of long, yellow needles, melting at  $140^\circ$ . Water decomposes its salts. By reduction it affords (1, 3)-diamido-benzene. **Para-nitraniline** (1, 4) forms needles or plates, melts at  $147^\circ$ , and yields (1, 4)-diamido-benzene.

When ortho- and para-nitranilines (not meta) are boiled with alkalis, they part with  $NH_3$ , and are converted into their corresponding nitrophenols,  $C_6H_4(NO_2)OH$ ; the di- and tri-nitranilines react even more readily.

**Dinitranilines**,  $C_6H_3(NO_2)_2.NH_2$ . The so-called *α*-dinitraniline is obtained from dinitrochlor- and dinitrobrom-benzene, also from *α*-dinitrophenol (its ether), when they are treated with ammonia in the heat. It melts at  $182^\circ$ , and by elimination of the  $NH_2$  yields ordinary dinitro-benzene (1, 3). Hence, its structure is (1, 2, 4— $NH_2$  in 1).

***β*-Dinitraniline** is obtained from *β*-dinitrophenol. It melts at  $138^\circ$ , and also yields (1, 3)-dinitro-benzene, hence its structure is (1, 2, 6—with  $NH_2$  in 1).

**Trinitraniline**,  $C_6H_2(NO_2)_3.NH_2$ , called Picramide, is obtained from picric acid through its ether, or by means of picryl chloride (p. 429). The latter reacts with ammonia, even in the cold. It forms orange-red needles, and melts at  $186^\circ$ . Its structure is analogous to that of picric acid (1, 2, 4, 6— $NH_2$  in 1). It forms picric acid when heated with alkalis:—



## ALCOHOLIC ANILIDES.

We find that, as in the amines of the fatty series, so in aniline, the hydrogen of the amido-group can be replaced by alcohol and acid radicals. The alkyl derivatives are formed in the same manner as the amines of the paraffin series (p. 122), by the action of the alkyl bromides and iodides upon aniline. This occurs mostly at ordinary temperatures. They can be directly produced by heating HCl-anilines with the alcohols to  $250^{\circ}$ . Alkyl chlorides are first produced, but they subsequently act upon aniline. The tertiary derivatives, *e. g.*,  $C_6H_5.N(C_2H_5)_2$ , combine further with the alkylogens, forming ammonium compounds, which moist silver oxide or lime converts into ammonium hydroxides:—



The alkyl anilines can, vice versa, be re-formed. Dimethyl aniline results when the ammonium hydrate or its haloid salts are distilled. This product, by further heating with HCl or HI to  $150^{\circ}$ , or by the distillation of its hydrochloride, regenerates methyl-aniline and aniline (p. 125). Toluidine and xyldine (p. 433) are produced when dimethyl-aniline hydrochloride is strongly heated. The aniline salts form ferrocyanogen salts with potassium ferrocyanide; these serve to separate the anilines (*Ann.*, 190, 184).

The methylated anilines are technically applied in the production of aniline dye-stuffs. They are formed on heating aniline, HCl-aniline and methyl alcohol to  $220^{\circ}$ . A better course is to conduct  $CH_3Cl$  into boiling aniline. Methyl and di-methyl aniline occur in both instances, together with unaltered aniline. Consult *Ber.*, 10, 591, and 795 for their separation and detection.

**Methyl Aniline**,  $C_6H_5.NH(CH_3)$ , is obtained pure from its nitroso-compound by reduction with tin and hydrochloric acid, or by the saponification of the acetyl derivative. The latter can be prepared from the sodium acetapilide,  $C_6H_5.N(Na).C_2H_3O$ , by treatment with methyl iodide (*Ber.*, 17, 267). It boils at  $190-191^{\circ}$ , has an odor resembling aniline and a sp. gravity at  $15^{\circ}$  of 0.976. Its salts (with HCl and  $H_2SO_4$ ) do not crystallize and dissolve in ether. Hence, dilute sulphuric acid in ethereal solution does not separate methyl aniline in crystalline form, as it does with aniline. Bleaching lime imparts no color. It forms with acetyl chloride or acetic anhydride the crystalline *acetyl derivative*,  $C_6H_5.N(CH_3).C_2H_3O$ , which melts at  $99.5^{\circ}$ , and boils at  $245^{\circ}$ . When methyl aniline is heated to  $330^{\circ}$  it is transformed into paratoluidine,  $C_6H_4(CH_3).NH_2$ .

**Nitroso-methyl-aniline**,  $C_6H_5 \left\{ \begin{array}{l} \\ CH_3 \end{array} \right\} N.NO$ , Phenyl methyl-nitrosamine (p. 433), is produced by the action of nitrous acid upon methyl aniline (also other secondary phenylamines), or better by  $KNO_2$  upon the solution of its HCl-salt. It



separates as a brown oil, which can be extracted with ether (*Ann.*, 190, 151). When distilled with steam it affords a yellow, aromatic-smelling oil, that cannot be distilled alone. It shows the nitroso reaction (p. 128) and does not combine with acids.  $\text{HgNa}$ , or zinc dust and acetic acid reduce it to methyl phenylhydrazine. It regenerates methyl aniline with zinc and sulphuric acid, tin and hydrochloric acid, or by gently heating with  $\text{SnCl}_2$ . Reaction with anilines or an alcoholic potash solution accomplishes the same (*Ber.*, 11, 757).

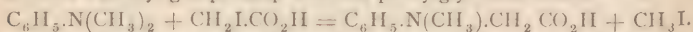
**Dimethyl Aniline**,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ , is obtained pure by distilling trimethyl-phenyl ammonium hydrate or its  $\text{HCl}$ -salt. The commercial article contains as much as 5 per cent. of methyl aniline. It is an oil boiling at  $192^\circ$  and solidifying at  $+5^\circ$ ; its sp. gr. is 0.955. Its salts do not crystallize. It forms an acetate,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\cdot\text{C}_2\text{H}_3\text{O}_2$ , with acetic acid; this decomposes again on distillation. Hypochlorites do not color it. It forms  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{I}$  with methyl iodide.

Dimethyl aniline is remarkable because in it, as in the phenols, there is a reactive H-atom in the benzene nucleus. The action of nitrous acid, or better, sodium nitrite, upon the  $\text{HCl}$ -salt (*Ber.*, 12, 253) produces the  $\text{HCl}$  salt of *p*-Nitroso-dimethyl Aniline,  $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ . This forms needles, which are not very soluble in water. The free base, separated from its salts by sodium carbonate, crystallizes in green, metallic-like laminae, melting at  $85^\circ$ . It yields dye-stuffs with phenols and anilines.  $\text{KMnO}_4$  and ferricyanide of potassium oxidize it to nitro-dimethyl-aniline. Warm, dilute caustic soda decomposes it into dimethyl aniline and paranitroso-phenol.

*p*-Nitro-dimethyl Aniline,  $\text{C}_6\text{H}_4(\text{NO}_2)\text{N}(\text{CH}_3)_2$ , is obtained in the oxidation of the nitroso-compound and by the action of fuming nitric acid (1 mol. upon dimethyl aniline in glacial acetic acid (10 parts) solution; it melts at  $162^\circ$ . **Dinitro-dimethyl Aniline** (1, 2, 4), obtained by further nitration, is also formed from *o*-dinitrochlorbenzene (p. 429), and trimethylamine (*Ber.*, 15, 1234); it melts at  $78^\circ$  and is easily decomposed by potash into dimethyl aniline and *o*-dinitrophenol.

*p*-Amido-dimethyl Aniline,  $\text{C}_6\text{H}_4(\text{NH}_2)\text{N}(\text{CH}_3)_2$ , dimethyl-paraphenylene diamine, is formed by the reduction of the nitroso- and nitro-compounds. It melts at  $41^\circ$  and boils at  $257^\circ$ . In acid solution it gives a dark blue coloration (methylene blue) with  $\text{H}_2\text{S}$  and ferric chloride, and answers as a sensitive reagent for hydrogen sulphide.

Other groups can replace a benzene hydrogen in dimethyl aniline. For example, an acid chloride (of dimethyl amido-benzoic acid) and ketones are produced by the action of  $\text{COCl}_2$ . Benzoyl chloride, benzyl chloride and chloro-oxalic ester react similarly, whereas by the action of chlor- or iod-acetic acids or their esters a methyl group is displaced and phenylglycocoll results:—



Dimethyl aniline, like the phenols, forms condensation products with aldehydes (oil of almonds, furfural, chloral, etc.); it combines with chlorides to yield phthaleines and green dye-stuffs, and with benzotrichloride,  $\text{C}_6\text{H}_5\cdot\text{CCl}_3$ , to form the so-called *malachite green*. A condensation of several benzene groups takes place, with the production of compounds which are allied to triphenyl methane and the aniline colors.

The so-called **Azylines** are tetra-alkyl-para-diamido-azobenzenes (see these):  $\text{R}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$ . They are formed when nitric oxide acts upon the tertiary anilines.

**Ethyl Aniline**,  $C_6H_5.NH.C_2H_5$ , boils at  $204^\circ$ ; its specific gravity at  $18^\circ$  is 0.954. Its *nitrosamine derivative*,  $C_6H_5.N(NO).C_2H_5$ , is a yellow oil with an odor resembling that of bitter almonds; it does not unite with acids and cannot be distilled (*Ber.*, 8, 1641).

**Methyl Ethyl Aniline**,  $C_6H_5.N(CH_3).(C_2H_5)$ , boils at  $201^\circ$ . Its compound with  $CHI_3$  is identical with dimethyl-aniline-ethyl iodide; methyl-ethyl aniline-ethyl iodide is also identical with diethyl aniline-methyl-iodide—an additional proof of the *equivalence of the five affinities of nitrogen* (p. 129, and *Ber.*, 17, 1325). Ethyl iodide is set free from all these ammonium iodides when they are heated with caustic potash.

**Diethyl Aniline**,  $C_6H_5.N(C_2H_5)_2$ , boils at  $213^\circ$ ; its specific gravity at  $18^\circ$  is 0.939. When heated with ethyl iodide it forms  $C_6H_5.N(C_2H_5)_3I$ , from which silver oxide separates the strong ammonium base,  $C_6H_5.N(C_2H_5)_3.OH$ ; the latter decomposes on distillation into diethyl aniline, ethylene and water. The *nitroso-compound*,  $C_6H_4 \begin{smallmatrix} \diagup N(C_2H_5)_2 \\ \diagdown NO \end{smallmatrix}$ , consists of large, green prisms, which melt at  $84^\circ$ , and yield nitroso-phenol and diethylamine, when boiled with dilute, caustic soda.

**Allyl Aniline**,  $C_6H_5.NH.C_3H_5$ , from aniline and allyl iodide, boils at  $208^\circ$ ; it yields quinoline,  $C_9H_7N$ , when distilled over heated lead oxide.

The derivatives with *divalent* alcohol radicals are formed the same as the alkyl anilines. **Methylene diphenyl-diamine**,  $(C_6H_5.NH)_2CH_2$ , from aniline and methylene iodide, is a thick liquid. Aniline yields **methylene aniline**,  $C_6H_5.N:CH_2$ , when acted upon by formic aldehyde. Bright crystals (*Ber.*, 17, 657).

**Ethylene-diphenyl-diamine**,  $(C_6H_5.NH)_2C_2H_4$ , from aniline and ethylene bromide, is crystalline, and melts at  $59^\circ$ . Isomeric **ethidene-diphenyl diamine**,  $(C_6H_5.NH)_2.CH.CH_3$ , is produced in the cold from aniline and aldehyde. It is amorphous. Similar compounds are produced with other aldehydes, e.g., valeral, acrolein, and furfurol. With chloral it gives **Trichlorethidene-diphenylamine**,  $(C_6H_5.NH)_2.CH.CCl_3$ , melting at  $100^\circ$ . **Acrolein-aniline**,  $C_6H_5.N:CH.CH:CH_2$ , is amorphous and yields quinoline,  $C_9H_7N$ , upon distillation.

#### PHENYLATED PHENYLAMINES (p. 432).

**Diphenylamine**,  $(C_6H_5)_2NH$ , is produced in the dry distillation of triphenyl rosaniline (Rosaniline blue), and is prepared by heating aniline hydrochloride and aniline to  $240^\circ$ :—



It results also upon heating aniline with phenol and  $ZnCl_2$  to  $260^\circ$ . It is a pleasant-smelling, crystalline compound, melting at  $54^\circ$ , and boiling at  $310^\circ$  (corrected). It is almost insoluble in water, but readily soluble in alcohol and ether. It is a very weak base, whose salts are decomposed by water. Nitric acid or sulphuric acid, containing nitrogen oxides, colors it a deep blue, and it serves in the preparation of various dye-stuffs. The *acridines* are obtained when diphenylamine is heated to  $300^\circ$  with fatty acids.

**Methyl Diphenylamine**  $(C_6H_5)_2N.CH_3$ , is formed by the action of methyl chloride upon diphenylamine. It boils at  $290-295^\circ$  ( $282^\circ$ ). **Diphenyl nitrosamine**,  $(C_6H_5)_2N.NO$ , is produced when ethyl nitrite acts on diphenylamine, or by the addition of  $HCl$ -diphenylamine to an acetic acid solution of potassium nitrite. Yellow plates of great brilliancy, melting at  $66.5^\circ$ . It dissolves with a deep blue color in concentrated sulphuric and hydrochloric acids.

**Nitrodiphenylamine**,  $C_6H_4(NO_2).NH.C_6H_5$ , from benzoyl nitro-diphenylamine, forms reddish-yellow needles, melting at  $132^\circ$ . **Para-Dinitrodiphenylamine**,  $[C_6H_4(NO_2)]_2NH$ , consists of yellow needles with a blue schimmer, and melts at  $214^\circ$ . Various **Tri-** and **Tetranitro-diphenylamines** are produced by the action of chlor-dinitro- and trinitro-benzenes upon aniline and nitro-anilines. **Hexanitrodiphenylamine**,  $[C_6H_2(NO_2)_3]_2NH$ , is formed by the direct nitration of diphenylamine and methyl diphenylamine. Yellow prisms melting at  $238^\circ$  (*Ber.*, 11, 845). It dissolves with a purple-red color, in the alkalies, forming salts. Its ammonium salt occurs in commerce as a brick-red powder, bearing the name *Aurantia*; it colors wool and silk directly a beautiful orange.

**Amido-diphenylamine**,  $C_6H_5.NH.C_6H_4(NH_2)$ , is formed by the reduction of its nitro-compound, and also by the decomposition of phenylamido-azobenzene and diphenylamidoazobenzene sulphonic acid (tropæoline oo) (see azo-compounds). It consists of laminae melting at  $61^\circ$ . **Para-Diamido-diphenylamine**,  $[C_6H_4(NH_2)]_2NH$ , is obtained in the reduction of the dinitro-compound, and by the decomposition of aniline black (together with para-phenylene-diamine). It crystallizes from water in leaflets, melting at  $158^\circ$ . It forms quinone when oxidized; ferric chloride or chromic acid colors it dark green. Its **tetramethyl compound** (melting at  $119^\circ$ ) is formed by the reduction of dimethyl phenylene green,  $C_{16}H_{19}N_3$  (see this). If oxidized in a solution containing  $H_2S$  it yields **methylene blue** (*Ber.*, 17, 224).

The diphenylamine amido-compounds are intimately related to the **safranines** (see these) from which they can be obtained by reduction.

**Dioxydiphenylamines**,  $C_6H_5.NH.C_6H_4(OH)_2$ , are formed on heating aniline with dioxybenzenes (resorcin, hydroquinone) and  $CaCl_2$  to  $250-270^\circ$ ; at higher temperatures, and with  $ZnCl_2$  we get diphenyl-phenylenediamines,  $C_6H_4.NH.C_6H_5)_2$ . (*Ber.*, 16, 2812). **Para-Dioxydiphenylamine** melts at  $70^\circ$ . **Dipara-dioxy-diphenylamine** is only known in its bromide,  $NH \begin{smallmatrix} \diagup C_6H_4.OH \\ \diagdown C_6H_4.Br.OH \end{smallmatrix}$ , and is closely allied to the indophenols (see these), as **Oxyamido-diphenylamine**,  $NH \begin{smallmatrix} \diagup C_6H_4.OH \\ \diagdown C_6H_4.NH_2 \end{smallmatrix}$ , is to the indoanilines.

**Thiodiphenylamine**,  $H_2N \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{smallmatrix} S$ , is produced in heating diphenylamine with sulphur to  $250^\circ$ . It crystallizes from alcohol in yellow laminae, melts at  $180^\circ$ , and boils near  $370^\circ$ . Fuming nitric acid converts it into a **dinitro-sulphoxide**,  $H_2N \begin{smallmatrix} \diagup C_6H_3(NO_2) \\ \diagdown C_6H_3(NO_2) \end{smallmatrix} SO$ . Reduction changes this to **diamido-thio-diphenylamine**,  $H_2N \begin{smallmatrix} \diagup C_6H_3(NH_2) \\ \diagdown C_6H_3(NH_2) \end{smallmatrix} S$ . When this product is oxidized with ferric chloride, it yields *Lauth's violet*.

Thio-diphenylamine is the starting-point for the preparation of dye-stuffs analogous to *Lauth's violet*, and the so-called *Methylene blue* (Caro). All contain sulphur. They were first made by oxidizing para-phenylene-diamines with ferric chloride in the presence of  $H_2S$  (*Lauth's reaction*). By their reduction (addition of 2H atoms), we get the leuco-dye-stuffs (see Rosaniline), which are derivatives of diamido thio-diphenylamine. When the latter are oxidized with  $FeCl_3$  (by

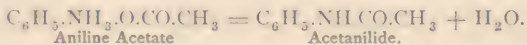
withdrawal of 2H-atoms), dye-substances are again formed, in which we must very probably assume a union of two nitrogen atoms (*Ber.*, 16, 2896, and 17, 611).

**Lauth's violet**, the prototype of these coloring substances, is obtained from phenylene-diamine by  $\text{FeCl}_3$  and  $\text{H}_2\text{S}$ ; its leuco-base,  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{S}$ , is diamido-thiodiphenylamine (see above). The dye-stuff (its HCl-salt) has the formula  $\text{C}_{12}\text{H}_9\text{N}_3\text{S}.\text{HCl}$ . **Methylene blue** is obtained from para-amido-dimethyl aniline (— dimethyl para-phenylenediamine, p. 438), with  $\text{FeCl}_3$  and  $\text{H}_2\text{S}$ ; it appears, also to result from tetramethyl-para-diamido-diphenylamine, p. 440, by the action of  $\text{FeCl}_3$  and  $\text{H}_2\text{S}$  (*Ber.*, 17, 224). Its HCl salt,  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}.\text{HCl}$ , occurs in commerce in blue laminae, under the name *Methylene blue* or *true blue*. It is the most stable blue for cotton. The reduction of this yields the leuco-base (its HCl-salt),  $\text{C}_{16}\text{H}_{19}\text{SN}_3.\text{HCl}$ , *Methylene white*, which probably is tetramethylated diamido-thiodiphenylamine (see above) (*Ber.*, 17, 619).

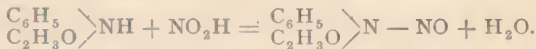
**Triphenylamine**,  $(\text{C}_6\text{H}_5)_3\text{N}$ , is obtained on heating dipotassium aniline (p. 432) or potassium diphenylamine with brombenzene. It crystallizes from ether in large plates, melts at  $127^\circ$ , and distils undecomposed. It dissolves in sulphuric acid, forming a violet, then a dark green color. It cannot form salts with acids.

#### ACID ANILIDES.

An atom of hydrogen of the amido- or imid-group in the primary and secondary anilines, can also be replaced by acid radicals. The resulting compounds are termed *anilides*, and are formed according to methods similar to those used with the acid amides of the fatty series (p. 207): by the action of acid chlorides or acid anhydrides upon the anilines, or by heating the organic salts of the latter:—

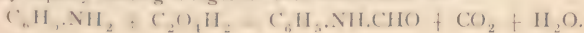


They are very stable derivatives; can usually be distilled without change, and also directly chlorinated, brominated and nitrated (p. 434). They are resolved into their components by warming with alkalis or heating with hydrochloric acid. The secondary anilides, like secondary alkylanilides (p. 432), afford *nitrosamines* by the action of nitrous acid:—



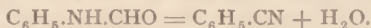
These show the nitrosamine reaction with phenol and sulphuric acid; but are less stable than the nitrosamines of the secondary anilines. Reducing agents break off their nitroso-group.

**Formanilide**,  $\text{C}_6\text{H}_5.\text{NH}.\text{CHO}$ , is obtained on digesting aniline with formic acid, or by rapidly heating it together with oxalic acid:—





It consists of prisms, readily soluble in water, alcohol and ether. It melts at  $46^{\circ}$ , and continues liquid for some time. Concentrated sodium hydrate precipitates the crystalline compound  $\text{C}_6\text{H}_5\text{N}(\text{CHO})\text{Na}$ , which is resolved by water into formanilide and  $\text{NaOH}$ . When formanilide is distilled with concentrated hydrochloric acid, benzonitrile is produced (small quantity):—



Dry  $\text{HCl}$  converts formanilide at  $100^{\circ}$  into diphenyl-methenylamidine (p. 451).  $\text{P}_2\text{S}_5$  changes it to *Thioformanilide*,  $\text{C}_6\text{H}_5\text{NH}\cdot\text{CS}\cdot\text{H}$ , which consists of white needles, melting at  $137^{\circ}$ , and decomposing at the same time into  $\text{H}_2\text{S}$  and phenylisocyanide,  $\text{C}_6\text{H}_5\text{NC}$ .

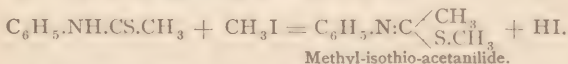
**Acetanilide**,  $\text{C}_6\text{H}_5\text{NH}\cdot\text{CO}\cdot\text{CH}_3$ , is produced by boiling (equal molecules) aniline and glacial acetic acid together for several hours (*Ber.*, 15, 1977); the solid, crystalline mass is then distilled. It melts at  $114^{\circ}$  and boils at  $295^{\circ}$ , without decomposition. It is soluble in hot water, alcohol and ether. Sodium converts it into sodium acetanilide,  $\text{C}_6\text{H}_5\text{N}(\text{Na})\cdot\text{C}_2\text{H}_3\text{O}$ . Heated with zinc chloride to  $270^{\circ}$ , it yields so-called *flavaniline*,  $\text{C}_{16}\text{H}_{11}\text{N}_2$ , a derivative of quinoline. Amidoacetophenone,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  (*Ber.*, 17, 1613), is formed on boiling aniline with acetic anhydride and zinc chloride.

Mono-substitution products (p. 434) are at first produced when chlorine, bromine and nitric acid act upon acetanilide; they yield mono-substituted anilines by saponification. *Monochloroacetanilide* (1, 4) melts at  $162^{\circ}$ , the dichlor at  $140^{\circ}$ ; both are formed by the action of bleaching lime (acidified with acetic acid) upon acetanilide. Monobrom-acetanilide (1, 4) melts at  $165^{\circ}$ ; the dibrom at  $78^{\circ}$ . p-Nitroacetanilide melts at  $207^{\circ}$  (Preparation, *Ber.*, 17, 222).

**Thioacetanilide**,  $\text{C}_6\text{H}_5\text{NH}\cdot\text{CS}\cdot\text{CH}_3$  (p. 210), crystallizes from water in needles, melting at  $75^{\circ}$ . It is soluble in alkalis, but is separated again by acids. *Alkylized* thioacetanilides, e. g.,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\cdot\text{CS}\cdot\text{CH}_3$ , are obtained from the acetyl compounds of the secondary anilines (like acetmethyl-anilide ( $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\cdot\text{CO}\cdot\text{CH}_3$ )) by heating them with  $\text{P}_2\text{S}_5$  (*Ber.*, 15, 528).

**Thioacet-methyl-anilide** melts at  $58\text{--}59^{\circ}$ , and boils at  $290^{\circ}$ .

The derivatives of hypothetical *isothioacetanilide*,  $\text{C}_6\text{H}_5\text{N}\cdot\text{C}\begin{smallmatrix} \text{CH}_3 \\ \text{SH} \end{smallmatrix}$  (p. 210), are isomeric with the above. They are obtained by the action of sodium alcoholate and alkyl iodides upon thioacetanilide (similar to formation of phenyl-isothio-urethanes, p. 446, and of phenyl-isothio-ureas, p. 448):—



The *methyl* compound boils at  $245^{\circ}$ , the *ethyl* at  $250^{\circ}$ . These decompose into aniline hydrochloride and thioacetic ester,  $\text{CH}_3\cdot\text{CO}\cdot\text{SR}$ , when shaken with hydrochloric acid.

#### ANILIDES OF DIVALENT ACIDS.

**Anilido-glycollic Acid**,  $\text{C}_6\text{H}_5\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , or Phenyl glycol,  $\text{CH}_2\begin{smallmatrix} \text{NH}\cdot\text{C}_6\text{H}_5 \\ \text{CO}_2\text{H} \end{smallmatrix}$ , is obtained from chlor- or brom- acetic acid by the action of aniline (2 molecules). It melts at  $126^{\circ}$ . **Methyl Phenyl-glycol**,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is produced from dimethyl-aniline and iod-acetic acid (p. 438).

The higher anilido-fatty acids, like *Anilido-propionic acid*, are similarly prepared from aniline and the brom- fatty acids. They can (their nitriles) also be

formed from the cyanhydrins of the aldehydes and anilines, *e. g.*, anilido-propionitrile,  $\text{CH}_3\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_5)\cdot\text{CN}$ , is obtained from  $\text{CH}_3\text{CH}\begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix}$  and aniline (*Ber.*, 15, 2034),

**Anil pyroracemic Acid**,  $\text{C}_6\text{H}_5\cdot\text{N}:\text{C}(\text{CH}_3)\cdot\text{CO}_2\text{H}$ , is formed from pyroracemic acid and aniline (2 molecules). Boiling water converts it into **anil-uvitonic acid**,  $\text{C}_{11}\text{H}_9\text{NO}_2$ , a derivative of quinoline, which yields methyl-quinoline,  $\text{C}_9\text{H}_8(\text{CH}_3)\text{N}$ , when distilled with lime (*Ber.*, 16, 2359).

By heating aniline and aceto-acetic ester to  $150^\circ$ , we get **Phenyl  $\beta$ -Imidobutyric Acid**,  $\text{C}_6\text{H}_5\cdot\text{N}:\text{C}\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_2\cdot\text{CO}_2\text{H} \end{smallmatrix}$ . This melts at  $81^\circ$ , and in contact with sulphuric acid (by elimination of water) is quietly transformed into  $\gamma$ -oxy-quinaldine (*Ber.*, 17, 541). Phenyl-hydrazine reacts similarly with aceto-acetic ester (*Ber.*, 17, 546). Nitrous acid converts phenyl-imido-butyric acid into **anil-isonitroso-acetone**,  $\text{C}_6\text{H}_5\cdot\text{N}:\text{C}\begin{smallmatrix} \text{CH}_3 \\ \text{CH}(\text{N}\cdot\text{OH}) \end{smallmatrix}$ , which melts at  $180^\circ$  (*Ber.*, 17, 1637).

#### ANILIDES OF OXALIC ACID.

**Oxanilide**,  $\text{C}_2\text{O}_2\begin{smallmatrix} \cdot \\ \text{NH}\cdot\text{C}_6\text{H}_5 \\ \text{NH}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}$ , diphenyl-oxamide, is obtained by heating aniline (2 molecules) with oxalic acid (1 molecule) to  $180^\circ$ . It consists of pearly leaflets, melting at  $245^\circ$  and boiling near  $320^\circ$ . It is readily soluble in benzene, and difficultly soluble in hot alcohol.

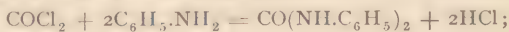
**Oxanilic Acid**,  $\text{C}_2\text{O}_2\begin{smallmatrix} \cdot \\ \text{NH}\cdot\text{C}_6\text{H}_5 \\ \text{OH} \end{smallmatrix}$ , is formed by heating aniline with excess of oxalic acid. It crystallizes in leaflets, dissolves in water, reacts acid, and conducts itself like a monobasic acid.

**Malonanilic Acid**,  $\text{CH}_2\begin{smallmatrix} \cdot \\ \text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5 \\ \text{CO}_2\text{H} \end{smallmatrix}$ , is produced by heating aniline and malonic acid to  $105^\circ$ .  $\text{PCl}_5$  converts it into a trichlor-quinoline (*Ber.*, 17, 740).

Similar anilides have been prepared from succinic, pyrotartaric, malic, tartaric, and other acids. **Phthalanile**,  $\text{C}_6\text{H}_5\cdot\text{N}\begin{smallmatrix} \cdot \\ \text{CO} \\ \text{CO} \end{smallmatrix}\cdot\text{C}_6\text{H}_4$ , formed by distilling aniline with phthalic anhydride, melts at  $205^\circ$ , and is adapted to further transpositions (*Ann.*, 210, 267).

#### ANILIDES OF CARBONIC ACID.

**Diphenyl urea**,  $\text{CO}\begin{smallmatrix} \cdot \\ \text{NH}\cdot\text{C}_6\text{H}_5 \\ \text{NH}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}$ , **carbanilide**, is formed by the action of phosgene gas on aniline (*Ber.*, 16, 2301):—



by union of carbanile (p. 444) with aniline:—



by action of mercuric oxide or alcoholic KOH upon diphenyl thio-urea (p. 447):—



and by heating aniline (3 parts) with urea (1 part) to  $150$ – $180^\circ$ :—

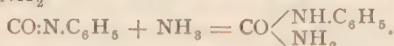


It is most readily obtained by heating carbanilamide with aniline to  $190^{\circ}$  (*Ber.*, 9, 820).

Carbanilide consists of silky needles, easily soluble in alcohol and ether, but difficultly soluble in water. It melts at  $235^{\circ}$  and distils at  $260^{\circ}$ . When boiled with alkalis it decomposes into aniline and urea. Triphenyl-guanidine is produced on heating it with sodium ethylate to  $220^{\circ}$ .

If  $\text{COCl}_2$  be conducted into the chloroform solution of diphenylamine, we obtain the *chloride of diphenyl urea*,  $(\text{C}_6\text{H}_5)_2\text{N}.\text{COCl}$ , which crystallizes in white laminae, melting at  $85^{\circ}$  and yielding at  $100^{\circ}$ , with alcoholic ammonia, unsymmetrical *diphenyl urea*,  $\text{CO} \begin{smallmatrix} \diagup \text{N}(\text{C}_6\text{H}_5)_2 \\ \diagdown \text{NH}_2 \end{smallmatrix}$ . Long needles, melting at  $189^{\circ}$ , and when distilled, yielding diphenylamine and cyanic acid. If the chloride be heated with aniline we get *Triphenyl urea*,  $\text{CO} \begin{smallmatrix} \diagup \text{N}(\text{C}_6\text{H}_5)_2 \\ \diagdown \text{NHC}_6\text{H}_5 \end{smallmatrix}$ , melting at  $136^{\circ}$ ; or *tetraphenyl urea*,  $\text{CO} \begin{smallmatrix} \diagup \text{N}(\text{C}_6\text{H}_5)_2 \\ \diagdown \text{N}(\text{C}_6\text{H}_5)_2 \end{smallmatrix}$ , if we employ diphenylamine. Crystals melting at  $183^{\circ}$ .

*Phenylurea*,  $\text{CO} \begin{smallmatrix} \diagup \text{NH.C}_6\text{H}_5 \\ \diagdown \text{NH}_2 \end{smallmatrix}$ , *Carbanilamide*, is obtained like the alkylic ureas (p. 505): by conducting vapors of cyanic acid into aniline;  $\text{CO:NH} + \text{C}_6\text{H}_5.\text{NH}_2 = \text{CO} \begin{smallmatrix} \diagup \text{NH.C}_6\text{H}_5 \\ \diagdown \text{NH}_2 \end{smallmatrix}$ ; and by the action of ammonia upon carbanil:—



It is best prepared by evaporating the aqueous solution of aniline hydrochloride and potassium isocyanide (*Ber.*, 9, 820). It forms needles easily soluble in hot water, alcohol and ether and melting at  $144\text{--}145^{\circ}$ . If boiled with caustic potash it breaks up into aniline, ammonia and cyanuric acid.

Esters of isocyanic acid convert aniline into alkylic phenyl ureas, *e. g.*,  $\text{CO} \begin{smallmatrix} \diagup \text{NH.C}_6\text{H}_5 \\ \diagdown \text{NH.C}_2\text{H}_5 \end{smallmatrix}$ , *ethyl phenylurea*.

*Glycolyl-phenylurea*,  $\text{CO} \begin{smallmatrix} \diagup \text{N}(\text{C}_6\text{H}_5).\text{CH}_2 \\ \diagdown \text{NH} \text{---} \text{CO} \end{smallmatrix}$ , *phenyl-hydantoïn* (p. 307), is obtained on heating phenylglycocoll (p. 442) to  $160^{\circ}$  with urea. It consists of needles, melting at  $191^{\circ}$ .

*Carbanilic Acid*,  $\text{CO} \begin{smallmatrix} \diagup \text{NH.C}_6\text{H}_5 \\ \diagdown \text{OH} \end{smallmatrix}$ , *phenyl carbamic acid*, is not known in a free state. Its esters, called *phenyl urethanes*, (p. 300) result in the action of chlorcarbonic esters upon aniline, or of carbanil upon alcohols:—



The *ethyl ester* melts at  $52^{\circ}$  and boils at  $237^{\circ}$ , decomposing partially into  $\text{CO:N.C}_6\text{H}_5$  and  $\text{C}_2\text{H}_5.\text{OH}$ , which reunite on standing. Diphenylurea is formed on heating with potash or with aniline.

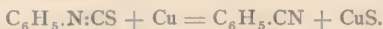
*Carbanile*,  $\text{CO:N.C}_6\text{H}_5$ , *phenyl isocyanate*, is produced in the distillation of oxanilide, or better oxanilic esters with  $\text{P}_2\text{O}_5$ . It may be most readily obtained by leading  $\text{COCl}_2$  into fused aniline-hydrochloride (*Ber.*, 17, 1284). It is a mobile liquid, boiling at  $163^{\circ}$  and has a pungent odor, provoking tears. Carbanile is perfectly analogous to the isocyanic esters in chemical deportment (p. 205). It affords diphenylurea with water. With ammonia carbanilamide,  $\text{CO} \begin{smallmatrix} \diagup \text{NH.C}_6\text{H}_5 \\ \diagdown \text{NH}_2 \end{smallmatrix}$ , is formed; with the amines we obtain corresponding alkyl compounds. Carbanile combines with alcohols, forming carbaulic esters.

**Phenyl Isocyanide**,  $C_6H_5.NC$ , phenyl carbylamine, is isomeric with benzonitrile,  $C_6H_5.CN$  (p. 246), and is produced by the action of chloroform on aniline in an alcoholic solution of KOH (*Ber.*, 10, 1096) or by the distillation of diphenyl-methenyl-amidine (p. 45), and of thioformanilide,  $C_6H_5.NH.CSH$ . It is a liquid resembling prussic acid, with pungent odor and boiling at  $167^\circ$  with partial decomposition. It is dichroic, being blue in reflected and green in transmitted light. Alkalies do not affect it, but acids convert it into aniline and formic acid. Heated to  $220^\circ$  it passes into isomeric benzonitrile,  $C_6H_5.CN$ . It combines with  $H_2S$ , forming thioformanilide (p. 442).

**Phenyl Mustard Oil, Sulpho-carbanile**,  $CS:N.C_6H_5$  (p. 240), is obtained by boiling diphenyl thio-urea (p. 447) with sulphuric or concentrated hydrochloric acid, or, what would be best, with a concentrated phosphoric acid solution (*Ber.*, 15, 986):—



and by the action of an alcoholic iodine solution (with phenyl guanidine, *Ber.*, 9, 812) or  $CSCl_2$  upon aniline. It is a colorless liquid, with an odor resembling that of mustard oil, and boils at  $220^\circ$ . It is converted into benzonitrile when heated with reduced copper or zinc dust:—



On this reaction is founded a procedure to replace the group  $NH_2$  by  $COOH$ , that is, to convert the anilines successively into thio-ureas, mustard oils, nitriles and acids. Benzonitrile (with aniline) is also produced by directly heating diphenyl thio-urea with zinc dust (*Ber.*, 15, 2505).

In all its reactions it is analogous to the mustard oils of the fatty series. If heated with anhydrous alcohols to  $120^\circ$ , or by the action of alcoholic potash, it is converted into phenyl-thio-urethanes (p. 302):—



It forms phenyl-thio-ureas with ammonia, the amines and the anilines.

**Phenyl-sulphocyanate**,  $C_6H_5.S.CN$ , is isomeric with phenyl mustard oil. It is formed when hydrosulphocyanic acid acts upon diazobenzene sulphate (see this), and cyanogen chloride upon the lead salt of methyl mercaptan:—



It is a colorless liquid, boiling at  $231^\circ$ , and in its reactions is analogous to the sulphocyanic esters (p. 239).

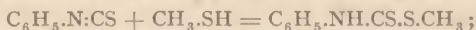
**Methenyl-amido Thiophenol**,  $C_6H_4 \begin{array}{l} \text{S} \\ \text{N} \end{array} \text{CH}$ , derived from ortho-amido thio-phenol,  $C_6H_4 \begin{array}{l} \text{SH} \\ \text{NH}_2 \end{array}$ , is a base, and is isomeric with phenyl sulphocyanate and phenyl mustard oils. See Amidophenols.

Derivatives of **Dithiocarbamic Acid** (p. 301).

**Phenyl Dithiocarbamic Acid**,  $CS \begin{array}{l} \text{NH.C}_6\text{H}_5 \\ \text{SH} \end{array}$ . Its potassium salt is formed when potassium xanthate (p. 299) is boiled with aniline and alcohol. It consists of golden yellow needles. When the acid is liberated from its salts it decomposes



into aniline and  $\text{CS}_2$ . Its *esters*—the normal dithio-urethanes (p. 302 and *Ber.*, 15, 563)—are produced by warming phenyl mustard oil with mercaptans:—



and from the alkyl compounds of diphenyl isothio-urea when heated with  $\text{CS}_2$  (p. 448). The *methyl ester* melts at  $87-88^\circ$ ; the *ethyl* (**Phenyl dithio-urethane**) at  $60^\circ$ .

When these dithio-urethanes are heated they decompose into phenyl mustard oil and mercaptans. They dissolve in alkalies, and on warming part with mercaptans (*Ber.*, 15, 1305). Completely alkylized dithio-urethanes, having the imide hydrogen replaced by alkyls, are formed the same as the mono-alkyl derivatives, *i. e.*, by heating alkylized diphenyl-amidinthioalkyls (p. 448) to  $150^\circ$  with  $\text{CS}_2$ .

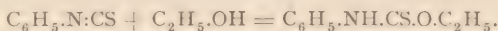
**Ethyl Phenyl dithiourethane**,  $\text{CS} \begin{smallmatrix} \diagup \text{N}(\text{C}_2\text{H}_5) \cdot \text{C}_6\text{H}_5 \\ \diagdown \text{S} \cdot \text{C}_2\text{H}_5 \end{smallmatrix}$ , melts at  $68.5^\circ$ , and boils at  $310^\circ$ . These compounds are very stable, no longer soluble in alkalies, and are not desulphurized by  $\text{HgO}$  or an alkaline lead solution. They form so-called addition products (*Ber.*, 15, 568, and 1308) with methyl iodide. Phenyl sulphurethane and diphenyl-thio-urea (p. 448) do the same.

An analogous compound is formed on heating diphenylamidin-thio-ethylene (p. 448) with  $\text{CS}_2$ . The product is called **Ethylene-Phenyl-dithiocarbamate**,  $\text{CS} \begin{smallmatrix} \diagup \text{N}-\text{C}_6\text{H}_5 \\ \diagdown \text{S}-\text{C}_2\text{H}_4 \end{smallmatrix}$  (*Ber.*, 15, 345).

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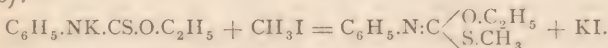
Derivatives of *Sulphocarbamic Acid*,  $\text{CS} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{OH} \end{smallmatrix}$ , *thio-carbaminic acid*,  $\text{CO} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{SH} \end{smallmatrix}$ , and the hypothetical *imidothiocarbonic acid*,  $\text{NH}:\text{C} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{SH} \end{smallmatrix}$  (p. 302).

**Ethyl Phenylsulphocarbamate**, **Phenyl-thiourethane**,  $\text{CS} \begin{smallmatrix} \diagup \text{NH} \cdot \text{C}_6\text{H}_5 \\ \diagdown \text{O} \cdot \text{C}_2\text{H}_5 \end{smallmatrix}$  (Phenyl xanthamide) (*Ber.*, 15, 1307), is formed by heating phenyl-mustard-oil with alcohol (*Ber.*, 15, 2164):—



It melts at  $71-72^\circ$ , and is resolved into phenyl-mustard-oil and alcohol when distilled. It is soluble in alkalies, and unites with  $\text{Hg}$ ,  $\text{Ag}$ , and  $\text{Pb}$ .

When alkyl iodides act upon these metallic compounds (not the free phenyl-sulphurethanes) we obtain *phenyl-isothiourethanes*, the alkyl derivatives of *phenyl imido thio-carbonic acid* (see above). The reaction is very probably analogous to that occurring with thioacetanilides (p. 442) and the phenyl sulpho-ureas (p. 448):—



The *methyl* derivative is a liquid, and boils with partial decomposition at  $260^\circ$ . The *ethyl* compound melts at  $30^\circ$  and boils at  $278-280^\circ$ .

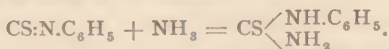
These alkyl derivatives are soluble in concentrated hydrochloric acid, and are precipitated by water. When heated with water they revert again to phenyl sulphurethane and alkyl chlorides; heated with dilute sulphuric acid to  $200^\circ$  aniline and thiocarbonic esters, *e. g.*,  $\text{CO} \begin{smallmatrix} \diagup \text{O} \cdot \text{C}_2\text{H}_5 \\ \diagdown \text{S} \cdot \text{CH}_3 \end{smallmatrix}$ , result.

The esters of *phenylthiocarbaminic acid* (see above), *e. g.*,  $\text{CO} \begin{smallmatrix} \diagup \text{NH} \cdot \text{C}_6\text{H}_5 \\ \diagdown \text{S} \cdot \text{CH}_3 \end{smallmatrix}$ , are obtained by heating the thio-alkyl-diphenylamidines (p. 448) with dilute sulphuric acid to  $180^\circ$  (*Ber.*, 15, 339).

The *methyl ester* melts at 83–84°; the *ethyl ester* at 73°. Warm alkalis resolve them into aniline,  $\text{CO}_2$  and mercaptans.

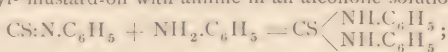
Another derivative of phenyl thio-carbaminic acid is the so-called glycolide of Phenyl-mustard-oil,  $\text{CO} \begin{array}{c} \diagup \text{N}(\text{C}_6\text{H}_5)_2 \text{CO} \\ \diagdown \text{S} \text{---} \text{CH}_2 \end{array}$  (p. 312), which is formed by heating phenyl-mustard-oil or phenyl thio-urethane with chloracetic acid and alcohol to 160°; also by boiling diphenylthiohydantoïn and (ortho) phenylthiohydantoïn (p. 449) with hydrochloric acid (*Ber.*, 14, 1663). It crystallizes from water in laminae, melting at 148° and decomposing, on boiling with baryta, into aniline,  $\text{CO}_2$  and thioglycollic acid.

**Phenylthiurea**,  $\text{CS} \begin{array}{c} \diagup \text{NH.C}_6\text{H}_5 \\ \diagdown \text{NH}_2 \end{array}$ , Sulphocarbanilamide (p. 310), is formed by the union of phenyl mustard-oil with ammonia:—

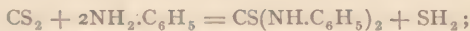


It crystallizes in needles, melting at 154°, and forms a double salt with  $\text{PtCl}_4$ . S is replaced by O and phenylurea formed on boiling with silver nitrate.

**Diphenyl-thiurea**,  $\text{CS} \begin{array}{c} \diagup \text{NH.C}_6\text{H}_5 \\ \diagdown \text{NH.C}_6\text{H}_5 \end{array}$ , sulphocarbanilide, is produced by the union of phenyl-mustard-oil with aniline in an alcoholic solution:—



it is also obtained by boiling aniline (1 molecule) with  $\text{CS}_2$  and alcoholic potash (1 molecule):—



the product is poured into dilute hydrochloric acid, the alcohol evaporated and the mass crystallized from alcohol.

Diphenylthiurea consists of colorless, shining leaflets, melting at 154° and readily soluble in alcohol. An alcoholic iodine solution converts it into sulphocarbanile and triphenyl-guanidine. When boiled with concentrated hydrochloric acid or phosphoric acid, it decomposes into phenyl-mustard-oil and aniline (p. 445); the mixed thiureas, containing two dissimilar benzene residues and resulting from the phenyl-mustard-oils and anilines (see above), undergo, under like treatment, a decomposition into two mustard-oils and two anilines (*Ber.*, 16, 2016).

S is replaced by O, and the product is diphenylurea, if diphenyl thiurea be boiled with alcoholic soda or mercuric oxide (p. 443); monophenyl thiurea, on the contrary, has  $\text{H}_2\text{S}$  eliminated and becomes phenylcyanamide (p. 311). In a benzene solution  $\text{HgO}$  produces carbodiphenylimide (p. 450).

In the action of alcoholic ammonia and lead oxide NH replaces S, forming diphenyl-guanidine (p. 311):—



under like circumstances they yield triphenyl-guanidines with anilines. Phenyl- and diphenyl-thiurea are soluble in alkalis, because metallic compounds are probably formed by the replacement of hydrogen of the imide-group (as in the case of thioacetanilide,  $\text{C}_6\text{H}_5.\text{NH}.\text{CS}.\text{CH}_3$  p. 442). If this be true they have not yet been isolated. Acids again set free the phenylureas.

**Tetraphenylthiurea**,  $\text{CS} \begin{smallmatrix} \diagup \text{N}(\text{C}_6\text{H}_5)_2 \\ \diagdown \text{N}(\text{C}_6\text{H}_5)_2 \end{smallmatrix}$ , is obtained by heating symmetrical tetra-phenylguanidine (p. 450) with  $\text{CS}_2$ . It crystallizes in long, shining needles, which melt at  $195^\circ$  (*Ber.*, 15, 1530).

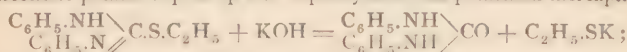
Derivatives of hypothetical *Isothiourea*,  $\text{NH}_2 \begin{smallmatrix} \diagup \text{N} \\ \diagdown \text{N} \end{smallmatrix} \text{C.SII}$  (Imidothiocarbamic acid, p. 309).

The diphenyl thioalkyl derivatives (their haloid salts) are obtained by the action of caustic alkali and alkyl iodides upon diphenylthiurea, or better by heating the latter with an alcoholic solution of the alkyl iodides (bromides) (*Ber.*, 14, 1489 and 1755):—

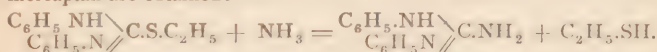


Alkalies set free the bases, which are soluble in alcohol and combine with 1 equivalent of acid to form crystalline salts.

The *methyl* compound melts at  $110^\circ$ ; the *ethyl* derivative at  $73^\circ$ . If heated with alcoholic potash it splits up into diphenylurea and potassium mercaptide:—



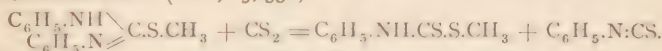
and when heated to  $120^\circ$  with alcoholic ammonia diphenyl-guanidine (p. 449) and mercaptan are obtained:—



The alkyl derivatives yield carbo-diphenylimide,  $\text{C}_6\text{H}_5 \cdot \text{N} \begin{smallmatrix} \diagup \text{C} \\ \diagdown \text{C} \end{smallmatrix}$  (p. 450), and mercaptan when distilled; and when heated to  $180^\circ$  with dilute sulphuric acid, they decompose into phenylthio-carbamic esters (p. 446), and aniline:—



If heated with  $\text{CS}_2$  to  $160^\circ$  the products are phenyl-mustard oil, and phenyl-dithiocarbamic esters (*Ber.*, 15, 338):—

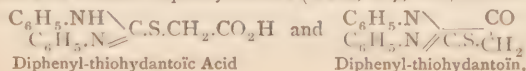


The last two decompositions are perfectly analogous to those of the amidines (p. 249).

When the diphenylamidine-thioalkyls are heated with alkyl iodides, their alkyl derivatives result *e.g.*,  $\text{C}_6\text{H}_5 \cdot \text{N}(\text{CH}_3) \begin{smallmatrix} \diagup \text{C.S.C}_2\text{H}_5 \\ \diagdown \text{C}_6\text{H}_5 \cdot \text{N} \end{smallmatrix}$ . These yield dialkyl dithio-urethanes with  $\text{CS}_2$  (p. 446).

Diphenylthiurea also reacts with benzyl chloride,  $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{Cl}$ . Ethylene bromide forms **Diphenylamidine-thioethylene**,  $\text{C}_6\text{H}_5 \cdot \text{N} \begin{smallmatrix} \diagup \text{C}_2\text{H}_4 \\ \diagdown \text{C.S} \end{smallmatrix}$ , which  $\text{CS}_2$  converts into ethylene-phenyl-dithiocarbamate (p. 446).

Chloroacetic acid converts diphenylthiurea (*Ann.*, 207, 128) into:—

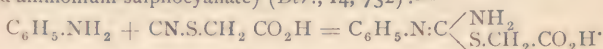


the diphenyl derivatives of so-called thiohydantoïn and thiohydantoïc acid (p. 312).

**Diphenylthiohydantoïn**,  $C_{15}H_{12}N_2SO$ , crystallizes from alcohol in leaflets, and melts at  $176^\circ$ . It decomposes, like the alkyl compounds (p. 448), when boiled with alcoholic potash, into diphenylurea, and thioglycollic acid,  $HS.CH_2.CO_2H$ . Boiling hydrochloric acid decomposes it into so-called glycolide of

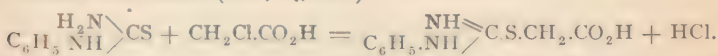
phenyl-mustard-oil,  $C_6H_5.N \begin{smallmatrix} \diagup CO \\ \diagdown CO.S.CH_2 \end{smallmatrix}$  (p. 447), and aniline.

**Phenylthiohydantoïc Acid**,  $C_6H_5.N \begin{smallmatrix} \diagup H_2N \\ \diagdown C.S.CH_2.CO_2H \end{smallmatrix}$  (Phenylamidine-thioglycollic acid), is produced (analogous to the formation of amidines from amines and cyanalkyls, p. 250) from aniline and sulphocyanacetic acid (or chlor-acetic acid and ammonium-sulphocyanate) (*Ber.*, 14, 732):—



It is soluble in alcohol, crystallizes in needles, and melts at  $148-152^\circ$ . Boiling dilute sulphuric acid decomposes it into phenylurea and thioglycollic acid.

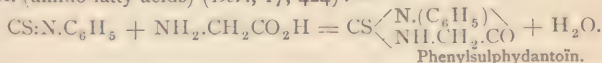
Isomeric, so-called (ortho)-**Phenylthiohydantoïc Acid**,  $C_9H_{10}N_2SO_2$ , is formed (analogous to thiohydantoïc acid (p. 312) from phenyl-thiourea and ammonium chlor-acetate (*Ber.*, 14, 1660):—



It is an amorphous mass, dissolving readily in alkalies and acids. The withdrawal of

water from it yields so-called (ortho)-**Phenylthiohydantoïn**,  $C_6H_5.N \begin{smallmatrix} \diagup NH \\ \diagdown C.S.CH_2 \end{smallmatrix} \begin{smallmatrix} \diagup CO \\ \diagdown \end{smallmatrix}$ , which melts at  $178^\circ$ , and is formed from thio-urea and chloracet-anilide,  $C_6H_5.NH.CO.CH_2Cl$ . Boiling dilute hydrochloric acid converts it into the glycolide of phenyl-mustard oil (p. 447); ammonia is liberated simultaneously.

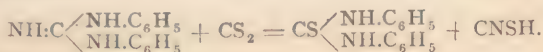
The real **Phenylsulphydantoïns**, corresponding to hydantoïn in constitution, and isomeric with the preceding so-called phenylthiohydantoïns (more correctly phenylamidine derivatives), are obtained by heating phenyl-mustard oil with glycocoll (amido-fatty acids) (*Ber.*, 17, 424):—



They are converted into the corresponding phenylsulphydantoïc acids on boiling with alcoholic potash, and are desulphurized by boiling with lead oxide.

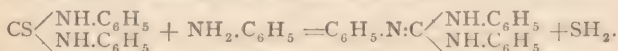
#### GUANIDINE DERIVATIVES (compare p. 250).

**Diphenyl-guanidine**,  $HN:C \begin{smallmatrix} \diagup NH.C_6H_5 \\ \diagdown NH.C_6H_5 \end{smallmatrix}$  (Melaniline), is produced by the action of  $CNCl$  upon dry aniline, and by digesting cyananilide,  $C_6H_5.NH.CN$ , with aniline hydrochloride. It crystallizes in long needles, melting at  $147^\circ$ . It is a mono-acidic base, forming crystalline salts.  $CS_2$  transforms it into sulpho-carbanilide and sulphocyanic acid, which combines with a second molecule of diphenyl guanidine:—



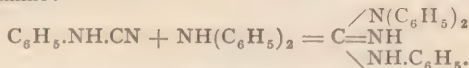


**$\alpha$ -Triphenyl-guanidine**,  $C_6H_5.N:C \begin{smallmatrix} \text{NH.C}_6\text{H}_5 \\ \text{NH.C}_6\text{H}_5 \end{smallmatrix}$ , is obtained on heating diphenyl-urea and diphenyl-thiurea, alone or with reduced copper, to  $140^\circ$ . It is most readily prepared by digesting diphenyl-thiurea and aniline, with litharge or mercuric oxide (or by boiling with an iodine solution):—



Triphenyl-guanidine crystallizes in rhombic prisms, melts at  $143^\circ$ , and is insoluble in water, difficultly soluble in ether, but readily in alcohol. It is a monacid base, and yields well crystallized salts. Heated with  $CS_2$  it is *vice versa* restored to diphenyl-thiurea and phenyl mustard oil.

Isomeric  **$\beta$ -Triphenyl-guanidine** is obtained by heating cyananilide with HCl-diphenylamine:—



It crystallizes in large plates, melting at  $131^\circ$  (see *Ann.*, 192, 9). It decomposes into diphenylamine, phenyl mustard-oil, and sulphocyanic acid when heated with  $CS_2$ .

Symmetrical **Tetraphenyl-guanidine**,  $NH:C \begin{smallmatrix} \text{N(C}_6\text{H}_5)_2 \\ \text{N(C}_6\text{H}_5)_2 \end{smallmatrix}$ , is produced by the action of  $CNCl$  upon diphenylamine at  $170^\circ$ . Its crystals are insoluble in water, and melt at  $130^\circ$ .

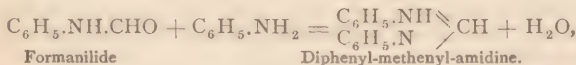
#### CYANAMID- AND CYAN- DERIVATIVES.

**Cyananilide**,  $C_6H_5.NH.CN$ , phenyl cyanamide (p. 247), is formed on conducting  $CNCl$  into a cooled alcoholic solution of aniline, and by digesting phenyl-thiurea with litharge. It crystallizes in long, colorless needles, which melt at  $36^\circ$ , and dissolve readily in alcohol and ether. It does not unite with acids. On standing it polymerizes to *Triphenyl-melamine*,  $(C_6H_5.N)_3H_3C_3N_3$  (p. 248), melting at  $162^\circ$ . It forms phenyl-thiurea with  $H_2S$ .

**Carbodiphenylimide**,  $C \begin{smallmatrix} \text{N.C}_6\text{H}_5 \\ \text{N.C}_6\text{H}_5 \end{smallmatrix}$ , is produced by the action of mercuric oxide upon diphenyl-thiurea in benzene solution, when  $H_2S$  is directly withdrawn (p. 447); or by the distillation of  $\alpha$ -triphenyl-guanidine, when aniline separates. It is a thick liquid boiling at  $330^\circ$ . It polymerizes upon standing, yielding a porcelainous mass, melting at  $170^\circ$ . When it absorbs water (boiling with alcohol) it yields diphenyl urea. It combines with  $H_2S$  to diphenyl thiurea, and with aniline to  $\alpha$ -triphenyl-guanidine.

Amidine derivatives (p. 249 and Benzenyl amidines).

In addition to the methods mentioned (pp. 249 and 250), we can also produce the phenylated amidines by permitting  $PCl_3$  or  $HCl$  to act upon a mixture of aniline with acid anilides:—



or by conducting  $HCl$  into anilides, or by heating the same with  $HCl$ -salts of the anilines (*Ber.*, 15, 208 and 2449). They are feeble bases, and yield salts with 1

equivalent of hydrochloric acid. When boiled with aniline they are separated into aniline and acid anilides.

**Diphenyl-methenyl-amidine** (Methenyldiphenyl diamine) results upon heating aniline with chloroform or formic acid to  $180^{\circ}$ , and by boiling phenyl-isocyanide,  $C_6H_5.NC$ , with aniline. It crystallizes from alcohol in long needles, melts at  $135^{\circ}$  and distils at  $250^{\circ}$ , with partial decomposition into  $C_6H_5.NC$  and aniline.

**Diphenyl-ethenyl-amidine melts at  $131^{\circ}$ .**

**Phenyl-ethenyl-amidine**,  $C_6H_5.N:C(NH_2).CH_3$ , from acetonitrile and  $HCl$ -aniline (p. 249) is a liquid.

We can also include here the so-called anhydro- and aldehydine bases (p. 455), which are obtained from the phenylene diamines of the ortho-series (see also **Benzenyl-amidine**).

## PHOSPHORUS COMPOUNDS.

There is a series of phosphorus compounds corresponding to the benzene amido-derivatives.

**Phenylphosphine**,  $C_6H_5.PH_2$ , is obtained by the action of hydriodic acid upon phosphenyl-chloride,  $C_6H_5.PCl_2$ . It is a liquid, boiling at  $160^{\circ}$  in a current of hydrogen, and possessing an extremely disagreeable odor. It sinks in water and is insoluble in acids. When exposed to the air it oxidizes to phosphenyl oxide,  $C_6H_5.PH_2O$ ,—a crystalline mass easily soluble in water. Phenylphosphine combines with  $HI$  to the iodide,  $C_6H_5.PH_2I$ , out of which water again separates phenylphosphine.

Phosphenyl chloride is formed by conducting a mixture of benzene and  $PCl_3$  vapors through tubes heated to redness, and by the action of  $AlCl_3$  upon benzene and  $PCl_3$ . It is a strongly refracting liquid, which fumes in the air, boils at  $222^{\circ}$ , and has a specific gravity 1.319 at  $20^{\circ}$ . It forms the *tetrachloride*,  $C_6H_5.PCl_4$ , with chlorine; this melts at  $73^{\circ}$ . With oxygen it yields the *oxychloride*,  $C_6H_5.PCl_2O$ , boiling at  $260^{\circ}$ . When the dichloride is heated with water we obtain phenyl-hypo-phosphorous acid,  $C_6H_5.PHO.OH$  (melting at  $70^{\circ}$ ), while the tetrachloride forms phenylphosphinic acid,  $C_6H_5.PO.(OH)_2$ , which melts at  $158^{\circ}$  (p. 122).

Phosphenyl chloride converts phenylphosphine into **Phospho-benzene**,  $C_6H_5.P:P.C_6H_5$ , corresponding to azobenzene,  $C_6H_5.N:N.C_6H_5$ .

**Diphenylphosphine**,  $(C_6H_5)_2PH$ , is obtained from diphenylphosphor-chloride. It is an oil, boiling at  $280^{\circ}$  (*Ber.*, 15, 801). *Diphenylphosphor-chloride*,  $(C_6H_5)_2PCl$ , from mercury diphenyl, and phosphenyl-chloride, boils at  $320^{\circ}$ .

**Triphenylphosphine**,  $(C_6H_5)_3P$ , is produced from  $C_6H_5.PCl_2$ , and brombenzene, or from  $PCl_3$  and brombenzene by the action of sodium (*Ber.*, 15, 1610); it crystallizes in large plates, melts at  $75^{\circ}$  and boils at  $360^{\circ}$ .

Toluene, xylene, and naphthalene afford similar phosphorus derivatives. Analogous arsenic compounds exist.

**Phenyl-silico-chloride**,  $C_6H_5.SiCl_3$ , is prepared by heating mercury diphenyl and  $SiCl_4$  to  $300^{\circ}$ . It is a liquid which fumes in the air and boils at  $197^{\circ}$ . Water decomposes it into the compound,  $C_6H_5.SiO.OH$ , which may be considered as benzoic acid in which the  $C$  carbon is replaced by silicon, hence it is called *Silico-benzoic acid*. Alcohol forms the triethyl ether,  $C_6H_5.Si(O.C_2H_5)_3$ , boiling at  $237^{\circ}$ . Zinc-ethyl converts the chloride into *triethyl-phenyl-silicide*,  $C_6H_5.Si.(C_2H_5)_3$ , boiling at  $230^{\circ}$ .

The arsenic and silicon compounds constitute the transition to the metallo-organic derivatives (p. 139); only those containing tin and mercury are known in the benzene series.

**Mercury-Phenyl** ( $C_6H_5$ )<sub>2</sub>Hg, is formed by treating brombenzene in benzene solution, for some time, with liquid sodium amalgam; the addition of some acetic ether facilitates the reaction (p. 143). It crystallizes in colorless rhombic prisms, melts at 120°, and can be sublimed. It assumes a yellow color in sunlight. It dissolves readily in benzene and carbon disulphide, but with more difficulty in ether and alcohol; in water it is insoluble. When distilled it decomposes for the most part into diphenyl, benzene and mercury. Acids decompose it with formation of benzene and mercury salts. Haloid compounds, *e. g.*,  $C_6H_5.HgI$ , are produced by the action of the halogens. Moist silver oxide converts them into hydroxyl derivatives, *e. g.*,  $C_6H_5.Hg.OH$ —a crystalline, very alkaline body, which separates ammonia from ammonium salts.

## ANILINE HOMOLOGUES.

These, like aniline, are obtained by the reduction of the nitro-derivatives of the homologous benzenes. Technically, the methylated homologues (toluidine, xylydene, cumidine) are prepared by heating dimethylaniline or methyltoluidine hydrochlorides to 300° (p. 432).

**Toluidines**,  $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown NH_2 \end{smallmatrix}$ . The three isomerides are formed by the reduction of the three corresponding nitrotoluenes. Crude, commercial toluidine (p. 429), obtained by reducing common nitrotoluene, consists of a mixture of solid para- and liquid ortho-toluidine; the former crystallizes out when brought to a low temperature.

To separate orthotoluidine from any para that continues in solution, the two are converted into acetyl compounds by digesting them with glacial acetic acid; in this new form they are dissolved in 4 parts concentrated acetic acid, and 80 parts of water are then added. The acetparatoluidine is precipitated, the ortho- body continues in solution. Technically, they are separated from each other (and from aniline) by the different behavior of their HCl-salts toward sodium phosphate (*Ber.*, 16, 908).

When the toluidines are directly oxidized they behave like the anilines and usually change to azo-compounds; should the amido-group, however, contain acid radicals, these acid toluides can be oxidized by  $MnO_4K$ , and by saponification yield amido-benzoic acids. Furthermore, the acid-toluides can be chlorinated, brominated, and nitrated the same as the anilides. The substituting negative group always arranges itself near the amido-group (in the ortho- position). Substituted toluidines are obtained by the saponification of these toluides.

**Paratoluidine** (I, 4), from solid paranitrotoluene, crystallizes in large plates, melts at 45°, and boils at 198°. Bleaching lime does not color it. The acetyl compound,  $C_7H_7.NH.C_2H_3O$ , melts at 147°, and boils near 306°. Formyl toluidine,  $C_7H_7.NH.CHO$ , is produced by distilling toluidine with oxalic acid (p.

441); when distilled with concentrated hydrochloric acid it yields (1, 4)-tolu-nitrile, which passes into terephthalic acid.

Methyl- and di-methyl-paratoluidine boil at 208°.

*Orthotoluidine* (1, 2) (*Pseudotoluidine*) does not solidify at -20°, and boils at 199°; its specific gravity at 16° is 1.00. Bleaching lime and hydrochloric acid color it violet, while a mixture of sulphuric and nitric acids gives it a blue color. Ferric chloride precipitates a blue compound (toluidine blue) from the HCl solution. Its acet-compound melts at 107° and when oxidized with  $\text{MnO}_4\text{K}$  and saponified yields ortho-amido benzoic acid (*Ber.*, 14, 263).

*Metatoluidine* (1, 3), from metanitrotoluene and metanitrobenzaldehyde (*Ber.*, 15, 2009), does not solidify at -13°, has a specific gravity 0.998 at 25°, and boils at 197°. Its acetyl compound melts at 65°.

*Ditolylamine*,  $(\text{C}_6\text{H}_4\cdot\text{CH}_3)_2\text{NH}$ , is produced like diphenylamine (p. 439) by heating HCl-toluidine with toluidine. It is a crystalline compound, boiling near 360°.

**Xylidines**,  $\text{C}_6\text{H}_3(\text{CH}_3)_2\cdot\text{NH}_2$ .

Five of the six possible isomerides are known. The commercial xylidine, obtained from dimethylaniline, serves for the preparation of red azo-dye stuffs, and consists chiefly of *amido-para-xylene*. It boils at 216-218°, and forms a difficultly soluble nitrate (*Ann.*, 215, 168). *Orthoxylidine* (1, 2, 4), from nitro-ortho-xylene, melts at 49°, and boils at 226° (*Ber.*, 17, 159).

**Amidotrimethyl-benzenes**,  $\text{C}_6\text{H}_2(\text{CH}_3)_3\cdot\text{NH}_2$ . The commercial product is made by heating xylidene hydrochloride with methyl alcohol: it serves for the preparation of red azo-dye-stuffs and contains cumidine and mesidine (*Ber.*, 16, 100, and 2895). *Cumidine* consists mainly of nitropseudocumene; it melts at 63°, boils at 235°, and forms a difficultly soluble nitrate. *Mesidine*, amido-mesitylene, is obtained from nitro-mesitylene, and boils at 227°.

Homologues of aniline with higher alkyls are easily obtained on heating aniline with fatty alcohols and  $\text{ZnCl}_2$  to 260-280° (p. 433); the alkyl assumes the para-position with reference to the amido group. *p-Amidoethylbenzene*,  $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)\cdot\text{NH}_2$ , also obtained from nitroethyl benzene (*Ber.*, 17, 767), boils at 214°. **Amidopropylbenzene**,  $\text{C}_6\text{H}_4(\text{C}_3\text{H}_7)\cdot\text{NH}_2$ , boils at 325°, the isopropyl compound at 217° (*Ber.*, 17, 1231). **Amidoisobutylbenzene**,  $\text{C}_6\text{H}_4(\text{C}_4\text{H}_9)\cdot\text{NH}_2$ , is easily obtained by heating aniline hydrochloride to 230° with isobutyl alcohol (*Ber.*, 14, 1472) and boils at 231°.

## DIAMIDO-COMPOUNDS.

The **diamidobenzenes** or **phenylene-diamines**,  $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , are formed by the reduction of the three dinitrobenzenes or nitro-anilines (p. 436) with tin and hydrochloric acid; they can be obtained, also, from the six diamidobenzoic acids,  $\text{C}_6\text{H}_3(\text{NH}_2)_2\cdot\text{CO}_2\text{H}$ , by the breaking-off of the carboxyl group. The three are soluble in water, especially when hot, crystallize in plates or laminae and on exposure to the air become colored. They are di-acidic bases, forming well defined salts.

*Ortho-diamido benzene* (1, 2) forms 4-sided plates, melts at 102° and boils at 252°. Ferric chloride or potassium bichromate imparts a dark red color to the HCl-solution. *Meta-diamido benzene* (1, 3), readily obtained from common dinitrobenze, melts at 63° and boils at 287°. Very dilute nitrous acid solutions are colored intensely yellow by it (ortho- and para- do not color); it can therefore be employed for the quantitative estimation of the former in aqueous solu-



tion (*Ber.*, 14, 1015). *Para* diamidobenzene (1, 4) melts at 147° and boils at 267°; manganese peroxide and sulphuric acid convert it into quinone on boiling.

Its *dimethyl* compound,  $C_6H_3 \begin{smallmatrix} \diagup N(CH_3)_2 \\ \diagdown NH_2 \end{smallmatrix}$ , has been already described as *p*-amidodimethyl-aniline (p. 438). The symm. *diethyl derivative*,  $C_6H_4(NH.C_2H_5)_2$ , is formed on digesting *p*-diamidobenzene with  $C_2H_5Br$ .

Diphenylated diamidobenzenes,  $C_6H_4(NH.C_6H_5)_2$ , are produced by heating resorcinol and hydroquinone,  $C_6H_4(OH)_2$ , with aniline and  $CaCl_2$  or  $ZnCl_2$  (see dioxydiphenylamine, p. 440).

**Triamidobenzenes**,  $C_6H_3(NH_2)_3$ . The *adjacent* (1, 2, 3) is obtained from triamidobenzoic acid (from chrysanisic acid). When pure it is colorless, melts at 103° and boils at 330°. It even reduces silver solutions in the cold, is colored violet then brown by ferric chloride and dissolves in sulphuric acid, containing a little nitric acid, with a deep blue color. The *unsymmetrical* (1, 2, 4) is obtained by the reduction of *α*-dinitroaniline (p. 436), and by the dissolution of chrysoïdine (*Ber.*, 15, 2197); it forms a crystalline mass and is colored a wine red by ferric chloride (*Ber.*, 17, Ref. 285).

**Diamidotoluenes, Toluylene-diamines**,  $C_6H_3(CH_3)(NH_2)_2$ . *α*-Diamidotoluene (1, 2, 4— $CH_3$  in 1), obtained by the reduction of *α*-dinitrotoluene, consists of long needles difficultly soluble in cold water, fusing at 99° and boiling at 280°.

*β*-Diamidotoluene (1, 3, 4— $CH_3$  in 1), with the  $2NH_2$  groups in the ortho-position, is obtained from nitroparatoluidine, forms scales that dissolve easily in cold water, melts at 89° and boils at 265°. *γ*-Diamidotoluene (1, 2, 3— $CH_3$  in 1), from nitro-ortho-toluidine, melts at 80°, boils at 270° and readily decomposes on exposure to the air. *ε*-Diamidotoluene (1, 2, 3 = 1, 3, 6— $CH_3$  in 1), from ortho- and meta-azo-amido-toluene (*Ber.*, 12, 2237), forms colorless leaflets, melting at 64° and yielding toluquinone if oxidized.

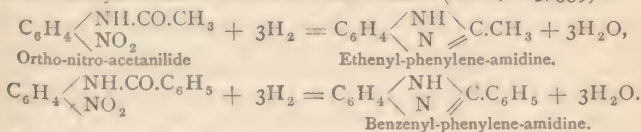
*Differences between the ortho-, meta- and para-diamines.* The para-diamines afford quinones, e.g.,  $C_6H_4(O)_2$ , when oxidized (with ferric chloride), whereas from the ortho-diamines (their HCl-salts) we have precipitated intensely colored compounds with metallic lustre, and of complicated composition. The meta-diamines yield brown-colored azo-dye substances—the chrysoïdines (p. 464), by their union with diazo-compounds. Nitrous acid converts the para-diamines into diazo-compounds, the meta-diamines (by converting a methyl group into a diazo, and by the union of two molecules) into chrysoïdines (see phenylene brown), and the ortho-diamines, by the condensation of the two amido-groups, yield the derivatives of the type of amidoazophenylene or azimidobenzene,  $C_6H_4 \begin{smallmatrix} \diagup NH \\ \diagdown N \end{smallmatrix} N$  (*Ber.*, 15, 1878 and 2195, 17, 147). In an analogous manner, the sulphocyanates of the orthodiamines condense to phenylenethiureas, like  $C_6H_4 \begin{smallmatrix} \diagup NH \\ \diagdown NH \end{smallmatrix} CS$  (*Ann.*, 221, 1); on the other hand, the cyanates of all three diamines afford phenylene-diureas (*Ber.*, 16, 592). The orthodiamines condense with acids and aldehydes, forming anhydrobases and aldehydines (see below).

*Condensation Products of the Orthodiamines.* The ortho-diamines, in which the  $2NH_2$ -groups occupy the ortho-position, are capable of forming peculiar compounds, in which the two amido-groups are joined by one carbon atom. They correspond, in all respects, to the ethenyl bases, or amidines (p. 450). They are crystalline, mon-acid bases, which are very stable, and generally afford well

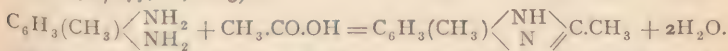
crystallized salts. They are incapable of forming acetyl compounds with acid chlorides or anhydrides. They combine with the alkyl iodides (1 and 2 molecules), producing ammonium-like compounds, from which corresponding hydroxides are obtained, by means of caustic potash.

The ortho-amido phenols and ortho-amido-thiophenols (see these) are also capable of yielding quite analogous anhydro-compounds. Those of the ortho-diamines are obtained :—

(1) By reducing the ortho-nitro acid anilides with tin and hydrochloric or acetic acid, the  $\text{NO}_2$ -groups being converted into  $\text{NH}_2$  and water eliminated at the same time—*Anhydrobases* of Hobrecker and Hübner (*Ann.*, 209, 339) :—



(2) By heating the ortho-phenylene-diamines with acids (acetic, formic, phthalic) (*Ber.*, 8, 677, 10, 1123) :—



The ortho-diamines afford similar derivatives with the aldehydes (benzaldehyde, furfurol, salicylic aldehyde)—**Aldehydine bases** of Ladenburg (*Ber.*, 11, 590) :—

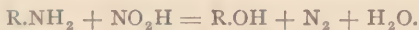


If the hydrochloric acid salts of the diamines (with  $2\text{HCl}$ ) be employed in this reaction, one molecule of  $\text{HCl}$  is set free, and the orthodiamines can thereby be readily distinguished from the meta- and para-diamines (*Ber.*, 11, 600, and 1650).

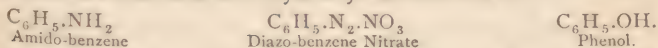
The ortho-diamines condense similarly with glyoxal,  $\text{CHO}.\text{CHO}$ , and with diketones, forming bases of the type of quinoxaline,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N:CH} \\ \diagdown \text{N:CH} \end{array}$  (see this), which stands in intimate relation to quinoline.

## DIAZO-COMPOUNDS.

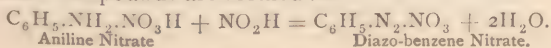
The amido-group is directly replaced by hydroxyl, when nitrous acid acts upon the primary amido-derivatives of the marsh-gas series (p. 125) :—



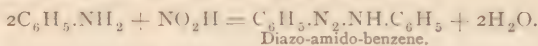
The benzeneamido-products, on the other hand, first yield intermediate compounds—the so-called diazo-compounds—which can be further transformed into hydroxyl derivatives :—



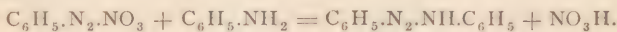
We obtain either diazo-or diazo-amido compounds, according to the conditions of the reaction. If nitrous acid (or its vapors) be permitted to act on the salts of amido-derivatives in aqueous solution, salts of the diazo-compounds are formed :—



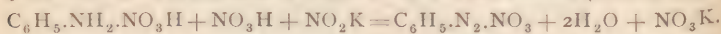
If, however, we act on the free amido-derivatives in alcoholic or ethereal solution, diazo-amido-compounds result :—



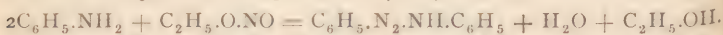
The diazo-compounds are formed at first, but combine with a second molecule of the free base and form diazo-amido-derivatives (p. 457):—



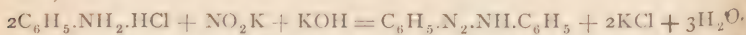
Instead of using free nitrous acid (its vapors) with amido-salts, we can obtain the diazo-derivatives more easily and in purer form, by dissolving the amido-compounds in two equivalents of dilute nitric or sulphuric acid, and then adding an equivalent amount of potassium or sodium nitrite to the solution (*Ber.*, 8, 1073):



To obtain the diazoamido-compounds add amyl nitrite or ethyl nitrite (1 molecule) to the ethereal solution of the amido-derivative (2 molecules) and allow the latter to evaporate over sulphuric acid (*Ibid*):—

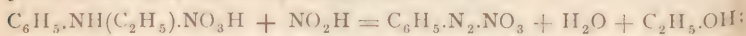


They are more easily prepared by adding the aqueous solution of  $\text{NO}_2\text{K}$  and  $\text{KOH}$  (1 molecule each) to the aqueous solution of the  $\text{HCl}$ -anilines (2 molecules):—



It is frequently recommended to substitute sodium acetate for alkalis (*Ber.*, 17, 641). In this case the reaction proceeds so that the diazo-compound is formed by  $\text{NO}_2\text{K}$  and 1 molecule  $\text{C}_6\text{H}_5\cdot\text{NH}_2\cdot\text{HCl}$ , and this immediately combines with the aniline liberated by the  $\text{KOH}$  and forms the diazo-amido-product (see amido-azo-benzene). All the above reactions must be executed in the cold.

Nitrous acid converts the secondary aniline bases into the same diazo-compounds, the alkyl group disappearing as alcohol:—



whereas nitroso-compounds result if potassium nitrite be employed (p. 437).

Further action of nitrous acid on the dissolved diazoamido-derivatives transforms them into diazo-compounds, and the latter, finally, by action of water, into phenols.

P. Griess first discovered the diazo-compounds, early in the '60's; their constitution was explained by Kekulé. They all contain the diazo-group of two nitrogen atoms, which on the one side replaces an atom of hydrogen in benzene, and on the other is attached to a monovalent group, as seen in the following formulas:—

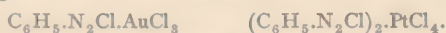
Diazobenzene nitrate,	$\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{O}\cdot\text{NO}_2$
“ sulphate,	$\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{O}\cdot\text{SO}_3\text{H}$
“ chloride,	$\text{C}_6\text{H}_5\cdot\text{N}=\text{NCl}$
Potassium diazobenzene,	$\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{OK}$
Silver “	$\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{OAg}$
Diazo-amidobenzene,	$\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$
Diazo-benzene sulphonate,	$\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{SO}_3\text{H}.$

This structure of the diazo-compounds is now fully proved by the existence of

the so-called tetrabrombenzene-diazosulphonic acid,  $C_6Br_4\langle\begin{smallmatrix} N_2 \\ SO_3 \end{smallmatrix}\rangle$  (*Ber.*, 9, 1537), and also by their relations to the hydrazines (*Ann.*, 190, 100).

Free diazo-benzene has not been as yet prepared pure, nor analyzed; it, however, corresponds to the formula  $C_6H_5.N=N.OH$ .

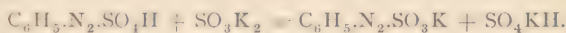
The diazo-chlorides can form double salts with auric and platinic chlorides, *e. g.* :—



The diazobromides also combine with two additional atoms of bromine, yielding *perbromides* :—

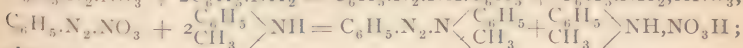
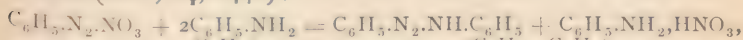


Potassium sulphite converts the sulphates into *diazosulphonic acids* :—



These pass into hydrazines when reduced.

The **Diazoamido-compounds** are also produced by the direct action of salts of the diazo-derivatives with primary and secondary anilines (*Ber.*, 14, 2448) :—

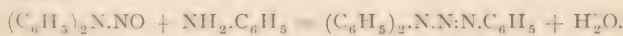


also :—

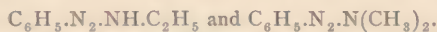


This explains their formation by the action of nitrous acid upon the free amido-compounds (p. 456).

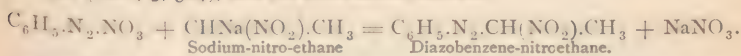
They can also be obtained by the action of the nitroso-amines upon the primary amido-bodies :—



It is not only with the primary and secondary anilines, but also with the primary and secondary (not tertiary) amines of the fatty series, with which the diazo-compounds are capable of combining, thus affording mixed diazoamido-compounds, *e. g.* :—



They react similarly with the sodium salts of the primary and secondary nitro-paraffins (*Ber.*, 9, 384), and the aceto-acetic esters :—



These new derivatives occupy a position between, as it were, the diazo- and azo-compounds.

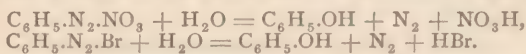
The salts of the diazo-compounds are mostly crystalline, colorless bodies, which speedily brown on exposure to the air. They are readily soluble in water, slightly in alcohol, and are precipitated



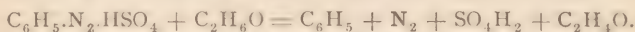
from the latter solution by ether. They are generally very unstable, and decompose with a violent explosion when heated or struck.

The diazo-derivatives are very reactive, and enter numerous, readily occurring reactions, in which nitrogen is liberated, and the diazo-group in the benzene nucleus directly replaced by halogens, hydrogen, hydroxyl, and other groups.

When the salts (sulphates are best) are boiled with water, the diazo-group is replaced by hydroxyl and phenols are produced :—

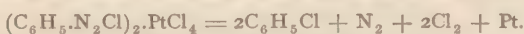


If alcohol be employed instead of water, then hydrogen will enter for the diazo-group, and hydrocarbons result. The alcohol is oxidized to aldehyde :—



Instead of first converting the amido- into the diazo-compounds, we can directly substitute  $\text{H}$  for  $\text{NH}_2$ , by adding them to alcohol saturated with  $\text{N}_2\text{O}_3$  (ethyl nitrite), and then apply heat. In this way diazo derivatives appear at first, but they are at once decomposed by the alcohol. Sometimes it is advisable to dissolve the amido-derivatives in a little concentrated sulphuric acid, lead nitrous acid into the solution, and then decompose with alcohol (*Ber.*, 9, 899).

Chlorbenzenes are formed, if the  $\text{PtCl}_4$ -double salts (p. 457) are heated alone, or what is better, with dry soda or salt :—

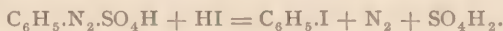


The replacement of the diazo-group by chlorine (conversion of the diazo-compounds into chlorbenzenes) is greatly facilitated by letting cuprous chloride, in  $\text{HCl}$ -solution, act on aqueous solutions of diazo-compounds (*Ber.*, 17, 1633).

When the diazo-perbromides are subjected to dry distillation, or boiled with alcohol (latter is oxidized to aldehyde), brombenzenes are formed :—



On digesting the diazo-salts with hydriodic acid, iodobenzenes separate :—

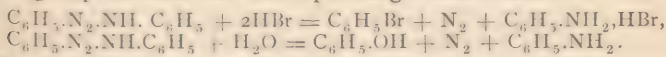


$\text{HBr}$  and  $\text{HCl}$  react similarly, providing the diazo-compounds contain additional negative groups (*Ber.*, 8, 1428, and 13, 964).

The diazo-group in the three diazocinnamic acids can be replaced by chlorine on boiling with concentrated  $\text{HCl}$ -acid (*Ber.*, 16, 2036).

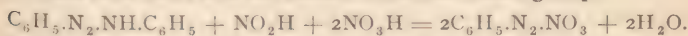
The diazo-amido-compounds *e. g.*,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , diazo-amidobenzene, are generally yellow-colored, neutral bodies which do not combine with acids. They are insoluble in water but dissolve in alcohol, ether and benzene. As a general thing they are more stable than the diazo-compounds, and do not often change

color on exposure to air; yet they undergo reactions analogous to those of the diazo-derivatives. In so doing they are resolved into their components; the amido-compound breaks off, while the diazo-group sustains the corresponding transformation:—



Phenol and aniline are also produced by boiling with concentrated hydrochloric acid.

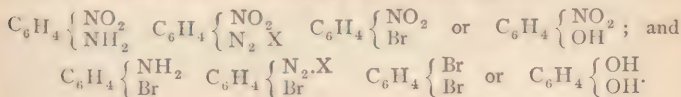
Nitrous acid converts the amido- into the diazo-group:—



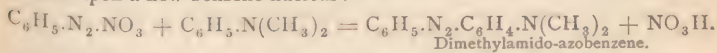
On boiling the alcoholic solution with sulphurous acid, the diazo-group is replaced by the sulpho-group, with formation of benzene-sulphonic acids (*Ber.*, 9, 1715):—



The diazo-derivatives of the substituted amides react similarly. Therefore the conversion through the diazo- or diazoamido-compounds is an excellent means of transforming amido-derivatives (and also nitro-) into the corresponding halogen- and oxy-compounds. Thus, we successively obtain from the three isomeric nitranilines the following derivatives belonging to the three series:—

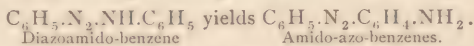


*Conversion of Diazo- into Azo-Compounds.* Besides the changes described the diazo-compounds exhibit other noteworthy reactions. While they form diazo-amido-derivatives with primary and secondary anilines (p. 457), they yield amido-azo-derivatives with tertiary anilines (p. 463), as the diazo-group encroaches upon a new benzene nucleus:—



They act in the same manner on the phenols, the phenolsulphonic acids and phenylenediamines,  $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , of the meta-series, producing various classes of coloring substances (the chrysoïdines and tropæolines), which belong to the group of azo-compounds (p. 462).

In an analogous manner, the diazo-amido compounds are transposed into azo-derivatives by simply standing or through the action of anilines (p. 463):—



For the relations of the diazo- to the hydrazine derivatives, see latter.

*Reactions of the Diazo-Compounds.* All, even the diazo-amido-compounds, give intense colorations (reaction of Liebermann), if added to a mixture of phenol and concentrated sulphuric acid. The nitroso-compounds (and also the nitrites) do the same. When an alcoholic solution of meta-diamido-benzene (or other meta-diamido derivatives) is added to a similar solution of the diazo-derivatives, red or brown colorations result; the diazoamido-bodies react under these conditions only after the addition of acetic acid (*Ber.*, 9, 1309). The resulting azo-derivatives belong to the chrysoïdines (p. 464).

**Diazobenzene Nitrate**,  $C_6H_5.N_2.NO_3$ , is formed by the action of nitrous acid upon an aqueous or alcoholic solution of aniline nitrate, or upon an ethereal solution of diazo-amidobenzene (in presence of nitric acid).

*Preparation.*—Pour a little water over the aniline nitrate. Cool the flask with ice from the outside and conduct in nitrous acid (from  $As_2O_3$  and  $HNO_3$ , specific gravity 1.35) until all the substance has dissolved and potassium hydrate, added to a little of the mixture, does not separate aniline. The dark solution is then filtered and alcohol and ether added, when diazobenzene nitrate is precipitated as a crystalline mass. Or, potassium nitrite may be allowed to act upon aniline nitrate (p. 426).

Diazobenzene nitrate forms long, colorless needles, and when dry is tolerably stable. It browns in moist air and decomposes rapidly. When heated it explodes with violence.

*Diazobenzene sulphate*,  $C_6H_5.N_2.SO_4H$ , is similarly obtained from aniline sulphate. It is advisable to add sulphuric acid (diluted with 2 volumes of water), alcohol (3 volumes) and then ether to the solution of diazobenzene nitrate. The sulphate then separates out on the bottom of the aqueous solution. After a second treatment with alcohol and ether, and evaporation under an air pump, it can be obtained crystalline. It consists of colorless needles or prisms, which dissolve readily in water. It explodes at  $100^\circ$ .

*Diazobenzene Sulphonic Acid*,  $C_6H_5.N_2.SO_3H$ . Its potassium salt is obtained by adding diazobenzene nitrate to a cold, neutral or feebly alkaline solution of potassium sulphite. The liquid solidifies to a crystalline mass of  $C_6H_5.N_2.SO_3K$  (*Ann.*, 190, 73). Acid potassium sulphite forms potassium benzene-hydrazine-sulphonate,  $C_6H_5.N_2.H_2.SO_3K$ .

*Diazobenzene Bromide*,  $C_6H_5.N_2Br$ , separates in white laminæ, if bromine be added to the ethereal solution of diazo-amido-benzene. Tribrom-aniline remains in solution. Ether precipitates the bromide from its alcoholic solution.

*Diazobenzene Perbromide*,  $C_6H_5.N_2Br_3$ , is precipitated from the aqueous solution of diazobenzene nitrate or sulphate, by bromine in  $HBr$ -acid or  $NaBr$ . It is a dark-brown oil, which quickly becomes crystalline. It is insoluble in water and ether, and crystallizes from cold alcohol in yellow laminæ. Continued washing with ether converts it into the diazo-bromide.

The *Platinum Double Salt*,  $(C_6H_5.N_2Cl)_2.PtCl_4$ , is precipitated in yellow prisms on adding a hydrochloric acid solution of  $PtCl_4$  to the solution of the nitrate or sulphate. It is difficultly soluble in water, and deflagrates when heated.

*Potassium Diazobenzene*,  $C_6H_5.N_2.OK$ , is separated, as a yellow liquid, from diazobenzene nitrate, by concentrated caustic potash. It crystallizes when evaporated in the water-bath, forming white, pearly leaflets, which dissolve readily in water and alcohol; the aqueous solution decomposes quickly.

*Silver Diazobenzene*,  $C_6H_5.N_2.OAg$ , is precipitated as a gray compound from the potassium salt by silver nitrate. It explodes very violently.

The compounds with mercury, lead, zinc, and other metals, are formed in a similar manner.

Acetic acid liberates *diazobenzene* (p. 457) from the potassium salt in the form of a heavy oil. It decomposes at once.

**Diazo-amido-benzene**,  $C_6H_5.N_2.NH.C_6H_5$ , is obtained by the action of nitrous acid on the alcoholic solution of aniline; by mixing diazobenzene nitrate with aniline, and by pouring a slightly alkaline sodium nitrite solution upon aniline hydrochloride (p. 456).

Dissolve aniline in alcohol (6-10 volumes), cool and conduct nitrous acid into the solution until a portion crystallizes on evaporation. The solution is then poured into water. A dark oil separates and soon becomes crystalline. It is washed out with cold, and then crystallized from hot alcohol.

Another method consists in adding sodium-nitrite (1 molecule), and then sodium-acetate (*Ber.*, 17, 641) to the hydrochloric acid (3 molecules) solution of aniline (2 molecules). Caustic soda forms amido-azobenzene at once.

Diazo-amidobenzene consists of golden-yellow, shining laminæ or prisms. It is insoluble in water, difficultly soluble in cold, but readily in hot alcohol, ether and benzene. It melts at  $91^{\circ}$ , and then explodes.

It does not combine with acids, although it forms a double salt,  $(C_{12}H_{11}N_3 \cdot HCl)_2 \cdot PtCl_4$ , with hydrochloric acid and  $PtCl_4$ . It crystallizes in reddish needles. When the alcoholic solution is mixed with silver nitrate, the compound  $C_6H_5 \cdot N_2 \cdot NAg \cdot C_6H_5$  separates in red needles.

When the alcoholic solution stands, especially in the presence of a little aniline-hydrochloride, the diazo-amidobenzene sustains an interesting transposition, resulting in the production of amido-azobenzene (p. 463).

**Diazobenzene-Ethylamine**,  $C_6H_5 \cdot N_2 \cdot NH(C_2H_5)$ , is formed when diazobenzene nitrate and ethylamine are mixed together. It is perfectly analogous to the dimethyl compound.

**Diazobenzene-Dimethylamine**,  $C_6H_5 \cdot N_2 \cdot N(CH_3)_2$ , is a yellow oil which affords very unstable salts with the acids. When their aqueous solution is heated phenol, nitrogen and dimethylamine are formed.

**Diazobenzene-Nitroethane**,  $C_6H_5 \cdot N_2 \cdot CH(NO_2) \cdot CH_3$  (p. 457), crystallizes in orange-colored leaves, melting at  $137^{\circ}$ . It is scarcely soluble in water, but readily in alcohol and ether. It behaves like an acid, dissolves with a blood-red color in alkalis, and forms salts with *two* equivalents of the bases.

**Diazobenzene Imide**,  $C_6H_5 \cdot N_3$ , is produced by the action of aqueous ammonia upon diazobenzene-perbromide:—

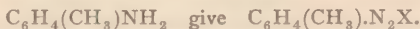


It is more readily obtained from phenylhydrazine. It is a yellow oil, insoluble in water, and can be distilled with steam or under diminished pressure. It dissolves unaltered in sulphuric and nitric acid. When zinc and hydrochloric acid act upon its alcoholic solution, it breaks up into aniline and  $2NH_3$ .

The substituted amidobenzenes, *e. g.*,  $C_6H_4Br \cdot NH_2$ , react like aniline with nitrous acid and afford perfectly analogous products. Free diazo-chlor- and diazobrom-benzene (p. 457) are crystalline compounds, but, owing to their instability, could not be analyzed. It is strange that the foreseen isomeric compounds, diazobenzene-amidobrombenzene,  $C_6H_4 \cdot N_2 \cdot NH \cdot C_6H_4Br$ , and diazobrombenzene-amido-benzene,  $C_6H_4Br \cdot N_2 \cdot NH \cdot C_6H_5$ , are identical (*Ber.*, 14, 2447). The high-substituted anilines, like trinitraniline,  $C_6H_2(NO_2)_3 \cdot NH_2$ , do not yield diazo-derivatives. The diamido-compounds, like phenylene diamine,  $C_6H_4 \cdot \begin{smallmatrix} \diagup NH_2 \\ \diagdown NH_2 \end{smallmatrix}$ , afford similar diazo-compounds (p. 454).



The aniline homologues, toluidine, xylidine, yield perfectly analogous diazo- and diazo-amido-compounds with perfectly similar properties. Thus, the three toluidines (ortho, meta, and para) yield three corresponding isomeric diazo-toluidines:—



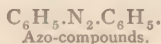
By the action of nitrous acid on the free toluidines we obtain *diazo-amido-toluidines*:—



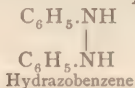
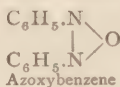
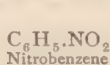
while the para-compound appears unaltered, the ortho- and meta- at once are transposed into the amido-azo-derivatives (p. 463).

### AZO-COMPOUNDS.

Like the diazo-derivatives, these contain a group consisting of two nitrogen atoms; in the former the  $\text{N}_2$  is combined with only one benzene nucleus; here it is attached on either side to benzene nuclei:—

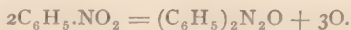


In consequence, they are far more stable than the former, and do not react with the elimination of nitrogen. They are classified as azoxy-, azo-, and hydrazo- compounds. They constitute, as it were, a transition from the nitro- to the amido- derivatives:—



They are obtained according to the following methods:—

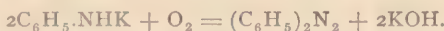
1. By reduction of the nitro-compounds in *alkaline* solution. Amido-derivatives are formed in acid solutions. By moderated reduction with an alcoholic potassium hydrate solution (or zinc dust and ammonium) azoxy-compounds are produced at first (the alcohol is oxidized to aldehyde):—



Stronger reducing agents (sodium amalgam in alcoholic solution, zinc dust) immediately form the azo- and hydrazo-derivatives. (All the nitrobenzene compounds, excepting nitronaphthalene, react similarly.)

2. By the *oxidation* of the primary amido-derivatives in alkaline solution with  $\text{MnO}_4\text{K}$  or potassium ferricyanide (*Ber.*, 9, 2098). Energetic reducing agents convert all the azo-derivatives into amido-bodies (p. 465).

3. By the action of sodium or potassium upon primary amido-compounds. Sodium amido-derivatives result and the oxygen of the air oxidizes them to azo-derivatives (*Ber.*, 10, 1802):—



Similarly, bromaniline yields azobenzene, as the bromine is reduced by the nascent hydrogen. The action of  $\text{C}_2\text{H}_5\cdot\text{NCl}_2$  upon aniline also affords azobenzene (*Ber.*, 16, 1048).

4. By the action of the nitroso-compounds upon the primary amines (see (Nitrosophenol):—



Reducing agents ( $\text{H}_2\text{S}$  also) further change the azoxy- to azo- and hydrazo-compounds; conversely, when the hydrazo- are oxidized (even in the air) they become azo-compounds.

The azoxy- and azo- derivatives are solids with a yellow to brown color, and do not unite with acids; the hydrazo-bodies are colorless and when in alcoholic solution, are easily changed by acids to isomeric diamido-diphenyls. Because of their stability, the azo-compounds can be directly chlorinated, nitrated, and sulphated.

On reducing the nitroazo-derivatives, we obtain the amido-azo compounds:—



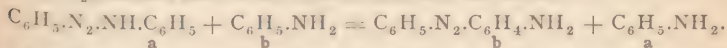
These are also obtained from the diazo-compounds by peculiar reactions:—

(1) By direct transposition of the diazoamido-compounds (p. 459):



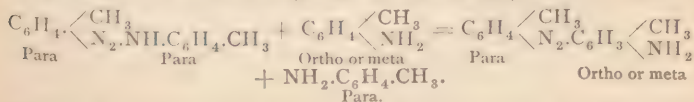
In the case of diazoamido-benzene, this transposition occurs on standing with alcohol, but more readily by the action of a slight quantity of aniline hydrochloride.

The group  $\text{NH}\cdot\text{C}_6\text{H}_5$  is eliminated from the diazo-compound, and the diazo-group,  $\text{N}_2$ , attaches itself to the benzene nucleus of the aniline:—



As aniline is regenerated here, a very slight quantity of it suffices to transform the diazo- into the azo-compound.

That the reaction indeed occurs as indicated, is verified by the knowledge that other (homologous) amido-compounds act similarly upon the diazo-amido-derivatives. Thus we obtain azo-derivatives from diazo amido-toluene, by action of the salts of meta- and ortho-toluidine (*Ber.*, 10, 664 and 1156):—

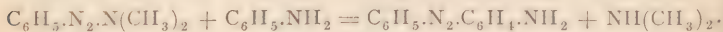


This would go to prove that the reaction only occurs readily, if in the reacting

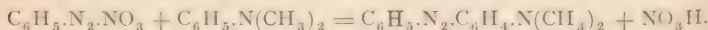
amido-compound the position in the benzene nucleus adjacent to the amido group in the para place be unoccupied: the diazo group,  $N_2$ , then arranges itself in the para-position referred to the  $NH_2$  of the amido-compound.

This explains, too, why only diazoamido-compounds are obtained from paratoluidine by nitrous acid, whereas the ortho- and meta-toluidines (in which the para-position is free) at once yield the amido-azo-derivatives (p. 462), because the diazoamido-bodies first produced can immediately transpose themselves. It was formerly thought, that in the production of azoamido-compounds, the diazo-group could invariably only enter the para-position (referred to the amido group). This, however, occurs only with special ease (in alcoholic solution). On heating diazoamido-paratoluene, dissolved in fused paratoluidine, to  $65^\circ$  with paratoluidine hydrochloride, a transposition will also take place with formation of *Amido-azoparatoluene*  $C_6H_4(CH_3).N_2.C_6H_3(CH_3).NH_2$ , (melting at  $118^\circ$ ), as the diazo-group enters the ortho-position (referred to amido group) (*Ber.*, 17, 77).

Diazobenzene-ethylamine and -dimethylamine (p. 461), react like the diazo-amido-compounds with aniline hydrochloride, the alkylamines breaking off at the same time:—

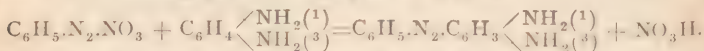


(2) By the action of the diazo-compounds upon the tertiary anilines (diazoamido-derivatives first result from the primary and secondary anilines, p. 457):—



In this reaction also, the  $N_2$ -group enters the position para with reference to the amido-group, and therefore dimethyl paratoluidine does not react (*Ber.*, 10, 526). Paradiazobenzene-sulphonic acid acts directly on the HCl-anilines, forming sulpho-acids of the amidoazo-compounds (*Ber.*, 15, 2184).

(3) By the action of the diazo-compounds upon the diamido-derivatives of the meta-series (p. 454), those of the ortho- and para-places not reacting (*Ber.*, 10, 389 and 654):—

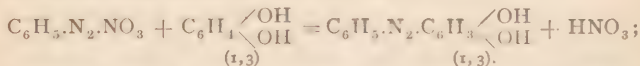


The resulting compounds are dye-stuffs, called *chrysoidines*, varying in color from orange to brown.

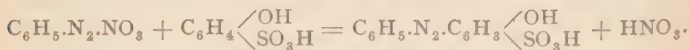
The diazo-derivatives react analogously with the phenols, forming *oxyazo-compounds*—with the monovalent phenols we have—



with the divalent phenols of the meta series:—

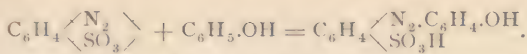


and with phenol-sulphonic acids and amidophenols (meta series):



Such azo-sulphonic acids can also be obtained by treating the azo-derivatives with sulphuric acid (see benzene sulphonic acids);

more readily by the action of diazo-sulphonic acids on amides or phenols:—

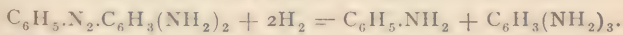


These oxyazo- and amido-azo-sulphonic acids are called *tropæolines*; many of them are applied as dye-stuffs.

The diazo-compounds act on the phenols in aqueous solution, but more readily when alkali is present (diazobenzene sulphate forms only phenyl ether or phenyl oxide,  $(\text{C}_6\text{H}_5)_2\text{O}$ , with aqueous phenol). Ordinarily the phenol derivative is dissolved in dilute alkalis and the aqueous diazo-chloride added. Occasionally it is advisable to apply sodium acetate instead of caustic alkalis (*Ber.*, 17, 641). Variations occur in the reaction sometimes, attributable to the quantity of alkali, whether it be in excess or in equivalent amount (*Ber.*, 17, 878). In the case of diazo-compounds and mono- and di-valent phenols two isomeric products, *a* and *β*, may arise—products soluble and insoluble in alkali (*Ber.*, 17, 877), (see Diazobenzene-disazoresorcinol, p. 466).

As in the amido-compounds, so in the phenols, the entering diazo-group prefers and assumes the para-position with reference to the hydroxyl group (p. 464); in the divalent phenols, like resorcinol, it takes the para-position referred to the *one* hydroxyl. Yet it can assume the ortho-position, *e. g.*, in para-cresol and *β*-naphthol (*Ber.*, 16, 2862, and 17, 350 and 876).

The amido-azo- and oxy-azo-compounds are yellow to brown in color, readily soluble in alcohol, and are crystalline. The salts with acids and alkalis constitute what are known technically as azo-coloring substances (p. 468). All azo-compounds dye cotton without the previous application of mordants. They are decolorized by reducing agents (tin and hydrochloric acid, zinc chloride, boiling with zinc dust, or upon digestion with ammonium sulphide), taking up four hydrogen atoms and being resolved into two amido-compounds. The azo-group,  $\text{N}=\text{N}$ , decomposes, each nitrogen atom remaining attached as  $\text{NH}_2$  to a benzene nucleus:—

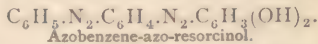


Such a decomposition occasionally takes place by heating with hydrochloric acid, indulines being simultaneously produced (*Ber.*, 17, 395). Consult *Ber.*, 15, 2812, upon the nomenclature of the azo-derivatives.

Nitrous acid converts the amido-azo-derivatives (like the amido-derivatives) into diazo-, *e. g.*,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ , azobenzene diazochloride, which, like simple diazo- and amido-derivatives, act on the phenols, forming so-called tetrazo-compounds, *e. g.*:—

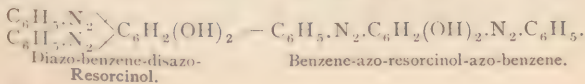


Azobenzene-azo-phenol



Azobenzene-azo-resorcinol.

Such compounds can also be obtained by a second introduction of two molecules of a diazo-compound into phenols (resorcinol), and are called *disazo-derivatives*:—



Diazo-benzene-disazo-Resorcinol.

Benzene-azo-resorcinol-azo-benzene.



Analogous compounds are also afforded with the anilines, and are called *azotriple bases* (*Ber.*, 16, 2028).

Another plan to obtain the tetrazo-derivatives employs the phenylene-diamines,  $C_6H_4(NH_2)_2$ , as points of departure, converting one and then the other amido- into a diazo-group, and finally combining the product with phenols; violet and blue azo-derivatives (*Ber.*, 17, 344 and 1350) are produced in this manner.

**Azoxybenzene**,  $(C_6H_5)_2N_2O$ , Azoxybenzide, is obtained by the reduction of nitrobenzene, or by the oxidation of amido-benzene (p. 462), the first being the preferable method.

Add 30 parts of pure nitrobenzene to a solution of 10 parts sodium in 250 parts methyl alcohol and boil for five or six hours, employing a return condenser. The unused methyl alcohol is distilled off and the residue washed with water (*Ber.*, 15, 866, 1515).

Azoxybenzene forms long, yellow needles, easily soluble in alcohol and ether, but not in water. It melts at  $36^\circ$ , and decomposes into azobenzene and aniline when distilled. It is converted into oxyazobenzene by digestion with sulphuric acid.

**Azobenzene**,  $(C_6H_5)_2N_2$ , Azobenzide, is formed by the action of sodium amalgam upon the alcoholic solution of nitrobenzene; on application of heat azobenzene distils over, whereas azoxybenzene remains. A simpler procedure is to distil azoxybenzene with iron filings, or to reduce nitrobenzene with zinc dust and caustic potash (*Ann.*, 207, 329). It forms orange-red, rhombic crystals, readily soluble in alcohol and ether, but difficultly soluble in water. It melts at  $68^\circ$ , and distils at  $293^\circ$ ; its vapor density confirms the molecular formula,  $C_{12}H_{10}N_2$ .

The nitration of the preceding yields *para-nitroazobenzene* and *para-dinitroazobenzene*,  $C_6H_4(NO_2)_2.N_2.C_6H_4(NO_2)_2$ .

**p-Oxyazobenzene**,  $C_6H_5.N_2.C_6H_4(OH)$ , Benzeneazophenol, is obtained on digesting diazobenzene nitrate with barium carbonate; by mixing the former with a solution of sodium phenol; by the action of para-nitrosophenol upon aniline acetate (p. 463), and by the action of concentrated sulphuric acid upon azoxybenzene (*Ber.*, 14, 2617). It crystallizes in orange-yellow needles, and melts at  $148^\circ$ .

**Di oxyazobenzenes**: **p-Azophenol**,  $C_6H_4(OH).N_2.C_6H_4(OH)$ , results: by fusing para- nitro- and nitroso-phenol with caustic potash; by the union of diazophenol nitrate with phenol, and from para-oxyazobenzene sulphonic acid (*Ber.*, 15, 3037). It consists of light brown crystals, and melts at  $204^\circ$ . **Benzene-azo-resorcinol**,  $C_6H_5.N_2.C_6H_3(OH)_2$ , is produced by adding diazobenzene nitrate or chloride to resorcinol in aqueous or alkaline solution. It forms red needles, melts at  $168^\circ$ , and dissolves with a yellowish-red color in alkalis. *Dibenzene disazo-resorcinol* ( $\gamma$ , insoluble in alkalis) forms at the same time; it results from the decomposition of diamido-resorcinol (*Ber.*, 17, 880).

The further action of a second molecule of diazobenzene chloride upon benzene-azo-resorcinol in alkaline solution, affords two isomeric **Dibenzene disazo-resorcinols**,  $C_6H_5.N_2.C_6H_3(OH)_2$ ,  $\alpha$  and  $\beta$ . The  $\alpha$ -compound is easily solu-

ble in aqueous alkalis, forms red needles, melts at  $214^{\circ}$ , and dissolves in  $\text{H}_2\text{SO}_4$  with a red color. The  $\beta$ -compound is insoluble in alkalis and dissolves in  $\text{H}_2\text{SO}_4$  with a dark blue color (*Ber.*, 15, 2816; 17, 880).

Compounds soluble and insoluble in alkalis are almost invariably produced by the union of diazo-derivatives with phenols. In the insoluble ones the  $\text{N}_2$ -group seems almost always to occupy the ortho-position as compared with hydroxyl (*Ber.*, 16, 2862).

The azobenzene-azo-resorcinols,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$ , are isomeric with the benzene-disazo-resorcinols. They form in the action of the diazo-chloride of amidoazo-benzene,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , upon resorcinol (*Ber.*, 15, 2817) (compare p. 465).

**Amido-azo-benzene**,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , is obtained in the reduction of nitro-azo-benzene with ammonium sulphide, and by the molecular transposition of isomeric diazo-amido-benzene (p. 463).

It is best prepared by the action of a mixture of potassium nitrite and caustic potash upon aniline hydrochloride; the diazo-amido-benzene first produced in the cold is transposed by digestion into amido-azo-benzene.

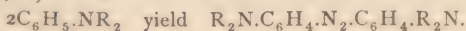
It crystallizes from alcohol in yellow needles or prisms, melts at  $123^{\circ}$ , and boils above  $360^{\circ}$ . It forms crystalline salts with one equivalent of acid; these are yellow and violet colored, and impart an intense yellow to silk and wool. The  $\text{HCl}$ -salt crystallizes from hydrochloric acid in blue needles or scales.  $\text{MnO}_2$  and sulphuric acid oxidize it to quinone. It is decomposed into para-diamido-benzene and aniline by tin and hydrochloric acid, digestion with ammonium sulphide, or boiling with hydrochloric acid (p. 465).

Commercial *Aniline Yellow* consists usually of amido-azo-benzene oxalate. The so-called *Acid Yellow* or *Pure Yellow* is a mixture of amido-azo-benzene sulphonic acids, and is prepared by the action of sulphuric acid on the amido-azo-compound, or by converting sulphanilic acid,  $\text{C}_6\text{H}_4(\text{SO}_3\cdot\text{H})\cdot\text{NH}_2$ , into the diazo-compound and then treating with aniline (*Ber.*, 15, 2184).

**Phenyl-amido-azo-benzene**,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , is isomeric with induline. It is produced from diazobenzene chloride and diphenylamine. It consists of golden-yellow leaflets, melting at  $82^{\circ}$ . Its sulphonic acid is tropæoline OO (p. 469).

**Diamido-azo-benzene**,  $\text{C}_{12}\text{H}_{12}\text{N}_4 = \text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2$ , Benzene-azo-phenylene-diamine, is produced by the action of diazo-benzene-nitrate upon meta-phenylene-diamine (p. 453), and consists of yellow needles, melting at  $117^{\circ}$ . Its hydrochloric acid salt occurs in trade under the name *chrysoïdine*, and dyes orange-red. Reduction changes it to aniline and unsymmetrical triamido-benzene,  $\text{C}_6\text{H}_3(\text{NH}_2)_3$ .

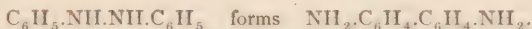
Symmetrical p-Diamido-azo-benzene,  $\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , has not been prepared. Its tetra-alkylic derivatives are the so-called *Azylines*. They are formed when nitric oxide acts upon the tertiary anilines (dialkylanilines) (*Ber.*, 16, 1416 and 2768):—



Dimethyl- and diethyl-aniline afford **dimethyl-aniline-azyline**,  $C_{16}H_{20}N_4$ , and **diethyl-aniline-azyline**,  $C_{20}H_{28}N_4$ . The azylines are red, basic dyes, which dissolve in hydrochloric acid with a purple-red and in acetic acid with an emerald-green color. By reduction (stannous chloride, tin and hydrochloric acid) they yield two molecules of dialkyl para-phenylene-diamine (p. 454). They are decomposed when heated to  $100^\circ$  with alkyl iodides (4 molecules); the products in this case are tetra-alkylic para-phenylene-diamines.

**Triamido-azo-benzene**,  $C_{12}H_{13}N_5 = H_2N.C_6H_4.N_2.C_6H_3 \begin{smallmatrix} \diagup NH_2 \\ \diagdown NH_2 \end{smallmatrix}$ , is formed when nitrous acid acts upon metaphenylene-diamine,  $C_6H_4(NH_2)_2$ . At first by transformation of an amido-group we obtain a diazo-compound, which further reacts on a second molecule of the diamine. Its hydrochloric acid salt is commercial *Phenylene Brown* (Manchester Brown, Bismarck-brown).

**Hydrazo-benzene**,  $C_{12}H_{12}N_2 = C_6H_5.NH.NH.C_6H_5$  (p. 457), is obtained by the action of  $H_2S$  and ammonia upon the alcoholic solution of azo-benzene, or by boiling the latter with zinc dust and alcohol. It is readily soluble in alcohol and ether, crystallizes in colorless plates, has an odor resembling that of camphor, melts at  $131^\circ$ , and further decomposes into azo-benzene and aniline. When its alcoholic solution is exposed to the air it oxidizes to azo-benzene. The mineral acids occasion in it an interesting transposition, resulting in the appearance of the isomeric, basic benzidine (diamido-diphenyl):—



Derivatives of benzidine are produced when it is heated with organic acids (*Ber.*, 17, 1181). Concerning additional formations of hydrazo-compounds and their transformations into benzidine derivatives, see *Ber.*, 17, 463.

**Diamidohydrazobenzene**,  $C_6H_4(NH_2).NH.NH.C_6H_4(NH_2) = C_{12}H_{14}N_4$ , formerly called *diphenine*, results from the action of ammonium sulphide upon para-dinitro-azo-benzene. It consists of yellow crystals, melts at  $145^\circ$ , and yields red salts with acids. Heated with ammonium sulphide it breaks up into 2 molecules of meta-diphenylene-diamine.

Below are mentioned some of the innumerable complicated azo-compounds, which are applied technically as *dyes*. They are either azo-amido-derivatives (azo-bases) which form salts with acids, or azo-phenol-compounds (azo-acids) (p. 465), yielding salts with bases. These salts represent the commercial dyes. In many cases the sulphonic acids of the azo-bases and azo-acids (the tropæolines, p. 465) are better adapted for the purpose, as their alkali salts are very stable, and usually afford dyes which dissolve readily in water. Arbitrary names are assigned these *dyes*, with the addition of the letters Y (yellow), O (orange), and R (red), whose number approximately expresses the intensity of the color. Recently violet and blue azo-dyes have been successfully prepared (mainly tetra-azo-compounds, p. 466).

**Tropæoline**, O or R (Chrysoïne, Chrysoiline),  $C_6H_4(SO_3H).N_2.C_6H_3(OH)_2$ , Resorcin-azo-benzene sulphonic acid, is obtained from para-diazo-benzene sulphonic acid and resorcinol (*Ber.*, **11**, 2195).

**Tropæoline**, OO (Orange IV),  $C_6H_4(SO_3H).N_2.C_6H_4.NH.C_6H_5$  (Diphenylamine-azo-benzene sulphonic acid), is obtained from diazobenzene sulphonic acid and diphenylamine). It is used as an indicator in alkalimetry (*Ber.*, **16**, 1989). By decomposition it yields sulphanilic acid,  $C_6H_4(NH_2).SO_3H$ , and amido-diphenylamine (p. 440).

**Tropæoline** OOO, No. I (Orange I), is formed from diazobenzene sulphonic acid and  $\alpha$ -naphthol. Tropæoline OOO, No. II (Orange II), is produced from diazobenzene sulphonate and  $\beta$ -naphthol (see Naphthols).

**Helianthine**, **Methyl Orange** (Orange III),  $C_6H_4(SO_3H).N_2.C_6H_4.N(CH_3)_2$ , Dimethylaniline-azo-benzene-sulphonic acid, is formed from diazobenzene sulphonic acid and dimethyl aniline (*Ber.*, **10**, 528). Consult *Ber.*, **17**, 1490, for another method of preparation. This and the analogous **ethyl orange** (from diethyl aniline) serve as delicate indicators in alkalimetry; mineral acids convert the alkaline orange-colored solution into a rose-red.  $CO_2$ ,  $H_2S$  and acetic acid do not act on it in the cold (*Chem. Zeit.* VI, 1249; *Ber.*, **7**, Ref. 185). In decomposition *helianthine* yields sulphanilic acid and para-amido-dimethyl aniline (p. 438), which is very well adapted for the preparation of methylene blue.

Various **Ponceaus** (R, RR, G, GG, etc.) are obtained by means of naphthol disulphonic acids from diazo-xylenes and diazo-cumenes (p. 453). **Bieberich Scarlets** are obtained from the sulphonic acids of amido-azo-benzene,  $C_6H_5.N_2.C_6H_4.NH_2$  (the chlorides) with  $\beta$ -naphthol. They are tetrazo-compounds (*Ber.*, **13**, 1838).

## SAFRANINES AND INDULINES.

Formerly these were included among the azo-dyes, because they were originally obtained from azo-compounds. They do, however, possess a different constitution from the latter, as they are not decomposed by reduction.

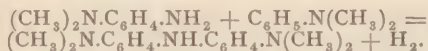
The *safranines* are a series of dyes varying from yellow to red, of the type,  $C_{18}H_{14}N_4$ , and are formed by oxidizing (with chromic acid) a mixture of a paradiamine with monamines (2 molecules, of which one must be a primary amine) (*Ber.*, **16**, 464 and 864). They result, too, from para-diamido-diphenylamine,  $H_2N.C_6H_4.NH.C_6H_4.NH_2$  (p. 440), by oxidizing a mixture of it with a primary monamine (1 molecule). When reduced the safranines take up two hydrogen atoms (*Ber.*, **17**, 226) and yield leuco-compounds, which can be reoxidized to safranines. Decomposition, such as noticed with the azo-compounds, occurs with difficulty. The deportment of safranines toward acids is characteristic. Their hydrochloric acid salts dissolve in water with a yellow-brown color, which by the addition of concentrated hydrochloric acid or sulphuric acid passes successively into violet, deep blue, dark green, and eventually light green; on diluting with water the reverse color phenomena appear.

**Phenylenesafranine**,  $C_{18}H_{14}N_4$ , Phenol safranine, is the lowest member of the safranines. It is formed from p-phenylene diamine and aniline. **Dimethyl-phenylene Safranine**,  $C_{18}H_{12}(CH_3)_2N_4$ , is obtained from dimethyl-para-phenylene diamine,  $C_6H_4(NH_2)N(CH_3)_2$ , or from nitroso-dimethyl aniline (p. 438) and aniline. **Tetra-methyl-phenylene Safranine**,  $C_{18}H_{10}(CH_3)_4N_4$ , results from dimethyl-para-phenylene diamine with dimethyl aniline and aniline. Perfectly analogous ethyl derivatives exist (*Ber.*, **16**, 470).



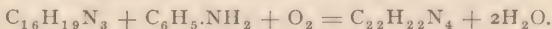
**Common Safranine**,  $C_{21}H_{20}N_4$ , **Toluylene Safranine**, is obtained from toluylene diamine and toluidine (2 molecules) (*Ber.*, 13, 307), or from amido-azo-toluene by heating ortho-toluidine hydrochloride (*Ber.*, 10, 875). Its HCl salt occurs in commerce as a brown paste or yellow-red powder, employed in cotton and silk dyeing. If heated with aniline it forms a violet dye,  $C_{27}H_{24}N_4$  (Phenylsafranine,  $C_{21}H_{19}(C_6H_5)_3N_4$ ), which is probably identical with **Mauveine**,  $C_{27}H_{24}N_4$  (Mauvaniline). The latter was the first aniline dye to prove valuable technically (Perkin, 1856), and is obtained by oxidizing aniline oil with potassium chromate and sulphuric acid.

The *blue* and *green* dyes, obtained by oxidizing para-phenylene diamines and amines (1 molecule) in the cold, are intermediate products. They are mostly unstable, and when heated change to safranines (*Ber.*, 16, 472). They include *phenylene blue*, *toluylene blue*, and so-called **dimethyl-phenylene green** (Bindschleider). The last is produced by the oxidation of dimethyl-phenylene diamine with dimethyl aniline in the cold (*Ber.*, 16, 865). Its HCl-salt,  $C_{16}H_{19}N_3 \cdot HCl$ , dissolves with a green color in water and colors silk yellowish-green. When it is reduced (addition of two hydrogen atoms) tetramethyl-diamido-diphenylamine,  $C_{16}H_{21}N_3$  (p. 440), is formed from it; and dimethyl-phenylene green is regenerated by its oxidation. Hence, tetramethyl-diamido-diphenylamine (the leuco-base of the green) is formed by the union of dimethyl-para-phenylene diamine with dimethyl aniline:—



In the production of the "green" from the latter (by elimination of two hydrogen atoms) it is probable that a union of two nitrogen atoms must be assumed.

By the oxidation of dimethyl phenylene-green with HCl-aniline tetramethyl-phenylene safranine (*Ber.*, 16, 869) is formed:—

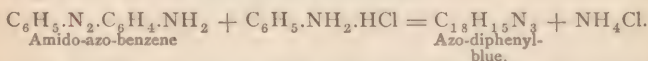


Here, likely, the imide hydrogen of diphenylamine is replaced by the aniline residue, so that the safranines are to be looked upon as triphenylamine,  $(C_6H_5)_3N$ , derivatives.

Very unstable **Phenylene Blue**,  $C_{12}H_{11}N_3$ , the product of the cold oxidation of para-phenylene diamine with aniline, yields para-diamido-diphenylamine by reduction (p. 440).

**Toluylene Blue**,  $C_{15}H_{18}N_4 = C_{15}H_{16}(NH_2)N_3$ , is formed from toluylene diamine (*a*-diamido-toluene, p. 454) by the action of nitroso-dimethyl aniline (*Ber.*, 12, 933). It dissolves in water with a blue-bottle color, and upon boiling yields **toluylene red**,  $C_{15}H_{16}N_4$ , which acts like *a safranine* (*Ber.*, 16, 475).

The *indulines* are violet and blue dyes, obtained by heating amido-azo-benzenes with HCl-anilines (with elimination of ammonia):—



Induline (azo-diphenyl blue) is more readily prepared from phenyl-amidoazo-benzene (p. 467) and aniline hydrochloride, whereby it is probable that the amido-azo-benzene first decomposes, forming a diamine (*Ber.*, 17, 76).

**Azo-diphenyl Blue**, aniline violet,  $C_{18}H_{15}N_3$  (isomeric with phenyl-amido-azo-benzene), is the prototype of the indulines. It is often produced in the oxidation of pure aniline, and is contained in the fuchsine fusion. Its hydrochloride is bright blue in color, and dyes wool and silk violet-blue.

**Aniline Black**,  $C_{30}H_{27}N_5$  (?), in all probability belongs to the indulines. It is formed by oxidizing aniline with potassium chlorate in the presence of copper

or vanadium salts. It is a dark green, amorphous powder, insoluble in all solvents. It is applied in calico-printing as a black dye, and in such a manner that it is first formed upon the fibre. By its reduction we obtain para-phenylene diamine and diamido-diphenylamine. The indophenols are closely related to the safranines; they are treated with the phenol-chlor-imides.

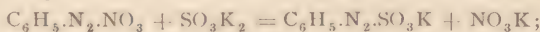
## HYDRAZINE COMPOUNDS.

The hydrazines stand in close relation to the diazo-compounds:—

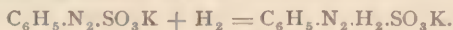


They are derivatives of diamide or hydrazine,  $\text{H}_2\text{N}\cdot\text{NH}_2$ , not known in a free state (p. 129). They are obtained:—

1. By the action of alkaline sulphites upon the diazo-derivatives. On allowing neutral potassium sulphite to act in the cold upon diazobenzene nitrate or hydrochloride, the yellow colored potassium salt of diazobenzene-sulphonic acid will be produced first (p. 460):—

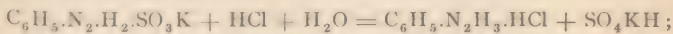


but should the primary potassium sulphite act at  $20-30^\circ$ , the diazo-sulphonic acid will be further reduced, and colorless potassium benzene hydrazine-sulphonate formed immediately:—



The yellow diazosulphonate can be reduced to the hydrazine compound by sulphurous acid, or, better, with zinc dust and acetic acid.

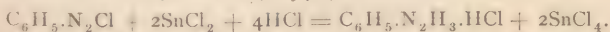
When the sulphonate is heated with hydrochloric acid hydrazine hydrochloride is produced:—



the alkalies separate the free hydrazine,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{H}_3$ .

*Preparation.*—In making phenyl hydrazine (benzene hydrazine) dissolve 20 parts of aniline in 50 parts of hydrochloric acid (sp. gr. 1.19) and 80 parts water, and then add the equivalent amount of sodium or potassium nitrite (dissolved in 2 parts water). The solution contains diazobenzene chloride,  $\text{C}_6\text{H}_5\cdot\text{N}_2\text{Cl}$ , and is gradually added to a cold solution of sodium sulphite (2 molecules); sodium phenyl hydrazine sulphonate then separates, but is mixed with the yellow diazo-sulphonate, which is completely reduced by digestion with zinc dust (with addition of acetic acid). The filtered, colorless solution of the hydrazine-sulphonate is boiled with concentrated hydrochloric acid ( $\frac{1}{3}$  volume), and the hydrazine separated by means of caustic soda (*Ann.*, 190, 78).

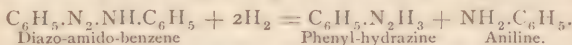
2. By the action of stannous chloride and hydrochloric acid upon the diazo-chlorides (*Ber.*, 16, 2976):—



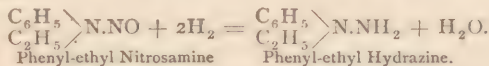
This procedure affords results which are especially good, if the hydra-

zine chloride (*e. g.*, naphthyl hydrazines) is difficultly soluble (*Ber.*, 17, 572).

3. By the reduction of diazo-amido-compounds in alcoholic solution with zinc dust and acetic acid, when they decompose into anilines and hydrazines:—



4. By the reduction of the nitroso-amines (pp. 128 and 443) with zinc dust and acetic acid:—



The hydrazines of the benzene series are mon-acid amines, combining directly with one equivalent of the acids to form crystalline salts.

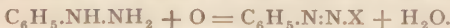
The *secondary phenyl-hydrazines* are obtained by the replacement of the hydrogen of the NH-group by alkyls. These products are identical with those obtained from the nitroso-amines by reduction. The latter are not further substituted, but unite with the alkylogens to yield ammonium compounds, *e. g.*, diethyl-phenylazonium bromide,  $\text{C}_6\text{H}_5\text{N}(\text{NH}_2)\text{C}_2\text{H}_5\text{Br}$ . When the acid chlorides act upon the primary hydrazines, one and two hydrogen atoms of the latter are replaced.

Nitrous acid replaces the imide hydrogen in the primary hydrazines, converting them into nitroso-derivatives, *e. g.*, phenylnitroso-hydrazine,  $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{NH}_2$ ; these give the nitroso reaction with phenol and sulphuric acid. The secondary hydrazines afford nitroso-amines by the elimination of the  $\text{NH}_2$ -group:—



Although the hydrazines are very stable in presence of reducing agents, they are readily oxidized and destroyed. They, therefore, reduce salts of the heavy metals and precipitate cuprous oxide from *Fehling's solution*; in this case the primary hydrazines react even in the cold, but the secondary not until heated.

The primary phenyl hydrazines may be readily reconverted into diazo-compounds; this is effected by the action of mercuric oxide upon their sulphonates:



The sulphonates (like  $\text{C}_6\text{H}_5\text{NHNH.SO}_3\text{K}$ ) (p. 471) are even more readily transposed. These salts can be obtained by heating the hydrazines with potassium pyrosulphate,  $\text{S}_2\text{O}_7\text{K}_2$ .

*Tetrazones*,  $\text{C}_6\text{H}_5\text{N}_3\text{N.N.NR.C}_6\text{H}_5$ , are produced by shaking the secondary phenylhydrazines with mercuric oxide (in chloroform solution) or with dilute ferric chloride.

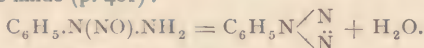
Phenyl hydrazine, like hydroxylamine,  $\text{HO.NH}_2$  (pp. 152 and 164), unites with aldehydes and ketones, and with aldehyde and ketonic acids, forming crystalline derivatives, *e. g.*,  $\text{C}_6\text{H}_5\text{NHN:N:CH.C}_6\text{H}_5$  and  $\text{C}_6\text{H}_5\text{NHN:N:C(CH}_3)_2\text{C}_6\text{H}_5$  (*Ber.*, 17, 572).

It also combines with the glucoses (dextrose, lævulose, galactose), with milk sugar and maltose; cane sugar is first inverted (*Ber.*, 17, 579).

Like aniline it combines with acetacetic esters, forming compounds, which upon condensation yield the *chinizine* derivatives (*Ber.*, 17, 546).

Phenylhydrazine also combines with the cyanhydrins of the aldehydes and ketones (same is true of aniline, p. 443), forming fatty-acid hydrazine-derivatives, *e. g.*,  $C_6H_5.N_2H_2.CH \begin{smallmatrix} \diagup CH_3 \\ \diagdown CO_2H \end{smallmatrix}$ , phenyl hydrazine-propionic acid (*Ber.*, 17, 1455).

**Phenylhydrazine**,  $C_6H_5.N_2H_3$ , is a colorless oil, boiling at  $233^\circ$ . It solidifies in the cold to plate-like crystals, which fuse at  $23^\circ$ . It is difficultly soluble in cold water, but readily in alcohol and ether. On exposure it rapidly becomes red to brown in color. The *nitroso-compound*,  $C_6H_5.N(NO).NH_2$ , forms yellowish leaflets and is readily converted by dilute alkalies, with separation of water, into diazobenzene imide (p. 461):—



**Methyl Phenylhydrazine**,  $C_6H_5 \begin{smallmatrix} \diagup CH_3 \\ \diagdown \end{smallmatrix} N.NH_2$ , boils at  $223^\circ$ , and becomes brown by oxidation in the air. When oxidized with an alkaline copper solution, it yields methyl aniline,  $C_6H_5 \begin{smallmatrix} \diagup CH_3 \\ \diagdown \end{smallmatrix} NH$ .

**Diphenyl Hydrazine**,  $C_6H_5 \begin{smallmatrix} \diagup CH_3 \\ \diagdown \end{smallmatrix} N.NH_2$ , from diphenylamine, is a non-solidifying oil, resembling methyl-phenyl-hydrazine, and is again changed to diphenylamine by oxidizing agents.

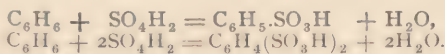
**p-Toluyldiazine**, from toluidine, melts at  $61^\circ$ , and boils with partial decomposition at  $240-244^\circ$ .

## SULPHO-COMPOUNDS.

The following are representatives of this class of derivatives:—

Benzene Sulphonic Acid,	$C_6H_5.SO_3H$ .
“ Sulphinic “	$C_6H_5.SO_2H$ .
“ Sulphone,	$(C_6H_5)_2SO_2$ .
“ Disulphoxide,	$(C_6H_5)_2S_2O_2$ .

The sulphonic acids of the benzene hydrocarbons (as well as of all other benzene derivatives) are very easily obtained by mixing (or digesting) the latter with concentrated or fuming sulphuric acid. The fatty acids afford like products with more difficulty (pp. 119 and 211):—

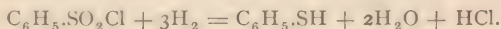


Chlorsulphonic acid,  $Cl.SO_2.OH$  (*Ber.*, 11, 2061), acts similarly to sulphuric acid. With it we can obtain the trisulpho-acids (*Ber.*, 15, 307). Further, some sulphonic acids can be obtained from the diazo-amido-derivatives by means of sulphurous acid (p. 459 and *Ber.*, 10, 1715).

The chloranhydrides of the sulphonic acids, *e. g.*,  $C_6H_5.SO_2Cl$ , are produced by letting  $PCl_5$  act on the acids or  $POCl_3$  upon the salts. Ammonia converts these into sulphamides,  $C_6H_5.SO_2.NH_2$ ,



and zinc and hydrochloric acid will reduce them to sulphydrates (thio-phenols) p. 119:—

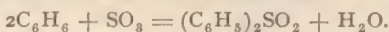


By replacing the chlorine in the sulpho-chlorides with hydrogen we get the *sulphinic acids*, in which the hydrogen atom is joined to sulphur (p. 112 and *Ber.* 13, 1281):—

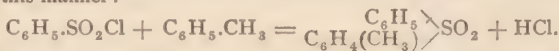


The sulphinic acids (their salts) can be prepared from the sulphonic chlorides and zinc alkyls, or by the action of sodium amalgam (better zinc dust) upon their ethereal solutions (p. 112 and *Ber.*, 13, 1273).

The benzene *sulphones* (sulpho-benzides) (p. 111) are obtained by the action of sulphuric anhydride (or  $\text{ClSO}_3\text{H}$ ) upon the benzenes:—

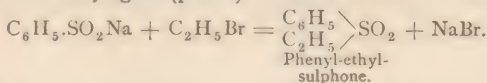


They are produced, also, in the distillation of the sulphonic acids (along with benzenes) and by the oxidation of the sulphides, *e. g.*,  $(\text{C}_6\text{H}_5)_2\text{S}$ . The *sulphoxides* (p. 110) are only known in combination with alkyls. The *sulphobenzides* are formed synthetically on heating sulphonic acid with benzenes and  $\text{P}_2\text{O}_5$ ; further, by the action of zinc dust or aluminium chloride (*Ber.*, 11, 2066) upon a mixture of the sulphonic chlorides and benzenes; mixed sulphones are also produced in this manner:—

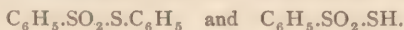


The same phenyl tolyl-sulphone results from benzene sulphonic acid and toluene as from toluene-sulphonic acid and benzene, which would prove that both groups are in union with sulphur and that the latter is hexavalent (*Ber.*, 11, 2181).

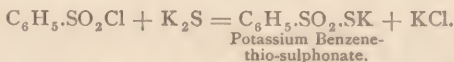
Mixed sulphones, containing alkyls, are prepared from the sodium sulphinates by the action of the alkylogens (p. 112):—



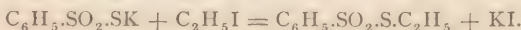
The so-called *Benzene-disulphoxides*, *e. g.*,  $(\text{C}_6\text{H}_5)_2\text{S}_2\text{O}_2$ , are esters of the benzene-thio-sulphonic acids:—



The latter are formed when alkaline sulphides act upon the chlorides of the sulphonic acids:—

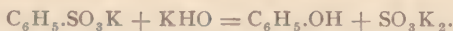


And by acting on these salts with alkylogens, esters of the thio-sulphonic acids (the disulphoxides) will be produced (*Ber.*, 15, 121):—



Phenyl esters, *e. g.*,  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_5$ , are obtained by oxidizing the thiophenols with nitric acid and by heating the sulphinic acids to  $100^\circ$  with water. The free thio-sulphonic acids decompose easily, like hyposulphurous acid, into sulphinic acids and sulphur.

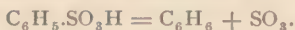
The benzene sulphonic acids are perfectly analogous to those of the fatty series. They are very stable and are not decomposed on boiling with alkalis. They afford phenols when fused with alkalis:—



When distilled with potassium cyanide (or dry yellow prussiate of potash) nitriles result:—

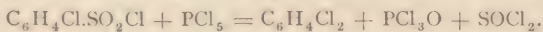


Hydrocarbons (together with phenyl sulphones) are formed when the free acids are subjected to distillation:—

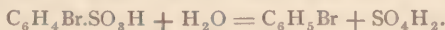


This rupture is more easily accomplished by heating the acids and HCl to  $150^\circ$ , or by distilling the ammonium salts (p. 412).

The sulphonic acids of the substituted hydrocarbons are obtained either by the action of sulphuric acid on the substituted hydrocarbons, or by the substitution of the sulphonic acids. In nitration the sulpho-group is often replaced by the nitro-group, just as on heating with  $\text{PCl}_5$  it is sometimes substituted by chlorine:

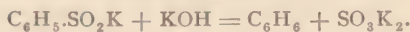


Most of the substituted benzene sulphonic acids have their sulpho-group replaced by hydrogen if they are heated to  $150$ – $200^\circ$  with concentrated hydrochloric acid:—



Nitro-benzenes and amido-benzenes result in like manner from the nitro-benzene- and amido-benzene-sulphonic acids (*Ber.*, 10, 317). Chlorine and bromine occasionally effect a like replacement of the sulpho-group (*Ber.*, 16, 617).

The sulphonic acids are not very stable, and when heated or allowed to stand some time over sulphuric acid they split up into sulphonic acids and *disulphoxides*. The air and oxidizing agents (especially  $\text{BaO}_2$ ) convert them into sulphonic acids. Their salts unite with sulphur, forming thio-sulphonates. When fused, they decompose into benzenes and alkaline sulphites:—



**Benzene-sulphonic Acid,  $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$ .** For its preparation equal parts of benzene and ordinary sulphuric acid are boiled for some time; or benzene is shaken with fuming sulphuric acid. Afterwards dilute with water and saturate with barium or lead carbonate. The free sulphonic acid is separated from its salts by means of  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{S}$ .

Benzene sulphonic acid crystallizes in small plates,  $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H} + \frac{1}{2}\text{H}_2\text{O}$ , which are readily soluble in alcohol and water, and deliquesce in the air. In its dry distillation the acid yields benzene and phenylsulphone (in slight quantity), and when fused with KOH phenol is produced.

The *barium salt*,  $(C_6H_5.SO_3)_2Ba + H_2O$ , forms pearly leaflets, and is difficultly soluble in alcohol. The *zinc salt*,  $(C_6H_5.SO_3)_2Zn + 6H_2O$ , crystallizes in six-sided plates.

**Benzene-sulpho-chloride**,  $C_6H_5.SO_2Cl$ , is an oil, insoluble in water, but dissolved by alcohol and ether. Its specific gravity at  $23^\circ$  is 1.378. It is crystalline below  $0^\circ$ , and boils at  $247^\circ$  with decomposition. It slowly reverts to the acid upon boiling with water. It may be obtained by gently digesting  $C_6H_5.SO_3Na$  with  $PCl_5$  and treating the product with water. If the chloride be digested with ammonia or ammonium carbonate we obtain—

**Benzenesulphamide**,  $C_6H_5.SO_2.NH_2$ , which crystallizes from alcohol in pearly laminae. It melts at  $149^\circ$  and sublimes. From the alcoholic solution silver nitrate precipitates  $C_6H_5.SO_2.NHAg$ . The amide hydrogen can also be replaced by acid or alcohol radicals.

**Benzene Sulphinic Acid**,  $C_6H_5.SO_2H$  (its zinc salt), is obtained by the action of zinc dust upon benzene sulphochloride. It crystallizes from hot water in large, brilliant prisms, and dissolves readily in alcohol and ether. It melts at  $69^\circ$ , and decomposes at  $100^\circ$ . In the air it oxidizes readily to benzene sulphonic acid. The *silver salt*,  $C_6H_5.SO_2Ag$ , is difficultly soluble in water.

**Phenylsulphone**,  $(C_6H_5)_2SO_2$ , sulphobenzide, is formed by the distillation of benzene sulphonic acid, and by the oxidation of phenyl sulphide,  $(C_6H_5)_2S$ . It is also obtained by the action of fuming sulphuric acid, or of  $SO_3$  upon benzene. It is very difficultly soluble in water and crystallizes in plates from alcohol. It melts at  $128-129^\circ$ , and distils without decomposition. It is converted into benzene-sulphonic acid when digested with concentrated sulphuric acid:—



When heated with  $PCl_5$ , or in a current of chlorine gas, it is decomposed according to the equation:—



$C_6H_5Cl$  and its addition products are also formed when chlorine acts upon it in sunlight.

**Benzene disulphoxide**,  $(C_6H_5)_2S_2O_2$  (p. 475), is produced along with benzene sulphonic acid on heating benzene sulphinic acid with water to  $130^\circ$ . It crystallizes in shining needles, and melts at  $130^\circ$ . It is insoluble in water but is readily dissolved by alcohol and ether.

**Benzene-disulphonic Acid**,  $C_6H_4 \begin{smallmatrix} \diagup SO_3H \\ \diagdown SO_3H \end{smallmatrix}$ . On heating benzene with fuming sulphuric acid to  $200^\circ C.$ , we get *meta* and *para*-benzene disulphonic acids, with the former in predominating quantity, but by prolonged heating it passes into the *para*-variety (*Ber.*, 9, 550). They can be separated by means of their potassium salts. *Metadisulphonic acid* (1, 3) is produced by heating parabrombenzenesulphonic acid with sulphuric acid to  $220^\circ$  and displacing the bromine with sodium amalgam, or from disulphanilic acid (p. 478) by means of the diazo-compound.

Orthobenzene disulphonic acid (1, 2) is formed from meta-amido benzene sulphonic acid by further introduction of the sulpho-group, and replacement of  $NH_2$ . The melting points of the sulphochlorides and sulphamides of the three isomeric disulphonic acids are:—

	Ortho	Meta	Para
$C_6H_4(SO_2Cl)_2$	$105^\circ$	$63^\circ$	$132^\circ$
$C_6H_4(SO_2.NH_2)_2$	$233^\circ$	$229^\circ$	$288^\circ$

The corresponding *dicyanides*,  $C_6H_4(CN)_2$  (see nitriles), are obtained by dis-

tillation with potassium cyanide or potassium ferrocyanide. When fused with potassium hydroxide, both *meta* and *para* acids yield resorcinol (metadioxybenzene); at lower temperatures metaphenol-sulphonic acid,  $C_6H_4(OH).SO_3H$ , results at first from both acids.

The **Chlorbenzene-sulphonic Acids**,  $C_6H_4Cl.SO_3H$ , are obtained from the chlorobenzene-sulphonic acids, by treating their diazo-compounds with hydrochloric acid. The (1, 4)-acid is also produced in the action of  $SO_4H_2$  upon  $C_6H_5Cl$ . The amide of the (1, 2)-acid melts at  $182^\circ$ ; the amide of (1, 3)-acid at  $148^\circ$ ; that of the (1, 4)-acid at  $143^\circ$ . The *chloride* of the (1, 4)-acid,  $C_6H_4Cl.SO_2Cl$ , melts at  $51^\circ$ ; it yields (1, 4)- $C_6H_4Cl_2$ , when heated with  $PCl_5$ .

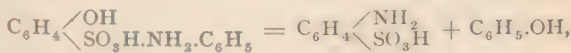
The **Brombenzene-sulphonic Acids**,  $C_6H_4Br.SO_3H$ , are obtained like the chlor-acids. The (1, 4)-acid is also formed on heating  $C_6H_5Br$  with  $SO_4H_2$  or  $SO_3HCl$ ; the (1, 3)-acid by heating benzenesulphonic acid with bromine to  $100^\circ$ , or by the action of Br upon  $C_6H_5SO_3Ag$  at ordinary temperatures. They are very deliquescent, crystalline bodies; the *para*-acid melts at  $88^\circ$ . All three yield resorcinol (1, 3), when they are fused with KOH. They form *dicyanides*,  $C_6H_4(CN)_2$ , by distilling their potassium salts with potassium cyanide or dry yellow prussiate of potash. Dicarboxylic acids are obtained from these.

**Nitrobenzene-sulphonic Acids**,  $C_6H_4(NO_2).SO_3H$ . If nitrobenzene be dissolved in fuming sulphuric acid, or benzene sulphonic acid in concentrated nitric acid, the three nitrobenzene sulphonic acids are produced—the (1, 4)-acid in largest quantity. For their separation they are converted into the amides,  $C_6H_4(NO_2).SO_2NH_2$ , which are then distilled. The free acids are very deliquescent crystalline masses. Their chlorides melt as follows: (1, 2) at  $67^\circ$ ; (1, 3) at  $60^\circ$ ; (1, 4) is a liquid. The amides fuse: (1, 2) at  $186^\circ$ ; (1, 3) at  $161^\circ$ ; (1, 4) at  $131^\circ$ . Ammonium sulphide reduces them to the corresponding amidobenzene sulphonic acids.

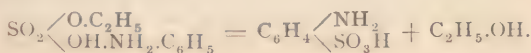
**Amidobenzene Sulphonic Acids**,  $C_6H_4(NH_2).SO_3H$ . They are produced by the reduction of the three nitrobenzene sulphonic acids with ammonium sulphide. The *para*-acid, commonly called *sulphanilic acid*, is obtained by heating aniline (1 part) with fuming sulphuric acid (2 parts) to  $180^\circ$  until  $SO_2$  appears. On diluting with water, the acid separates as a crystalline mass. Its diazo-compounds are changed by HBr into the corresponding brombenzene-sulpho-acids; by HCl into chlorbenzene sulphonic acids.

The three amido-benzene sulphonic acids are very difficultly soluble in water, alcohol and ether. The (1, 2)-acid either crystallizes in anhydrous rhombohedra, or in four-sided prisms containing  $\frac{1}{2} H_2O$ ; these do not effloresce. The (1, 3)-acid crystallizes in delicate needles or in prisms with  $1\frac{1}{2} H_2O$ , which effloresce. The sodium amido-benzene-sulphonates yield acetyl derivatives with acetic anhydride (*Ber.*, 17, 708).

**Sulphanilic Acid** (1, 4) is obtained by heating (1, 4)- and (1, 2)-aniline-phenol-sulphonate:—



or aniline ethyl sulphate to  $200^\circ$ :—





It yields aniline and not amidophenol when fused with caustic potash. It crystallizes from hot water in rhombic plates with 1 molecule  $H_2O$ ; these effloresce in the air. They are soluble in 112 parts  $H_2O$  at  $15^\circ$  (*Ber.*, 14, 1933). It affords considerable quantities of quinone, when oxidized with  $MnO_2$  and  $H_2SO_4$  or chromic acid.

Nitrous acid transforms sulphanilic acid into **Diazobenzene-sulphonic Acid**,  $C_6H_4 \begin{smallmatrix} \diagup SO_3 \\ \diagdown N:N \end{smallmatrix}$ . This is almost insoluble in cold water and crystallizes from hot water in colorless needles. To prepare it sulphanilic acid is dissolved in caustic soda, mixed with an equivalent amount of sodium nitrite, and the solution poured into dilute sulphuric acid. When heated to  $80^\circ$  with water the diazo-acid becomes paraphenol-sulphonic acid,  $C_6H_4 \begin{smallmatrix} \diagup SO_3H \\ \diagdown OH \end{smallmatrix}$ ; heated with absolute alcohol it affords benzene-sulphonic acid. Hydrogen sulphide causes it to revert to sulphanilic acid. It combines to tropæolines with anilines and phenols (p. 469).

Ortho- and meta- amidobenzene-sulphonic acids are also altered by nitrous acid, in aqueous or alcoholic solution, to diazo-derivatives,  $C_6H_4 \begin{smallmatrix} \diagup N_2 \\ \diagdown SO_3 \end{smallmatrix}$ . Diazoamido-compounds are not produced here, as with the amido-benzoic acids (*Ber.*, 10, 1536).

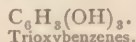
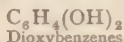
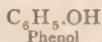
**Disulphanilic Acid**,  $C_6H_3(NH_2)(SO_3H)_2$  (1, 4, 2 —  $NH_2$  in 1), is obtained by protracted heating of sulphanilic acid to  $180^\circ$  with concentrated sulphuric acid. The replacement of the amido-group affords metabenzene-disulphonic acid (p. 476).

**Toluene Sulphonic Acids**,  $C_6H_4(CH_3).SO_3H$ . It is chiefly the para-compound, together with some ortho- and meta- (*Ber.*, 17, Ref. 283), which is produced by the solution of toluene in sulphuric acid or by the action of chlor-sulphonic acid upon it. The *chloride* of the *para*-acid is solid and melts at  $69^\circ$ , that of the ortho-acid is liquid. When fused with alkali the para-acid affords para-cresol and para-oxybenzoic acid, the ortho-acid, however, ortho-cresol and salicylic acid. When the former is oxidized with a chromic acid mixture it yields parasulphobenzoic acid, whereas the latter is destroyed.

When toluene is heated with fuming sulphuric acid it yields *toluene-disulphonic acids*. The higher benzene sulphonic acids will be described in connection with their respective hydrocarbons.

## PHENOLS.

The mono-, di- and tri-valent phenols are derived by the replacement of hydrogen in the benzenes by hydroxyls:—

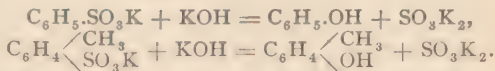


The phenols correspond to the tertiary alcohols, as they yield neither acids nor ketones upon oxidation. Their acidic nature, distinguishing them from alcohols, is governed by the more negative nature of the phenyl group (p. 404). The following are the more general and most important methods of forming them:—

1. By the action of nitrous acid upon the aqueous solution of the amido-compounds, or by decomposing the diazo-derivatives with boiling water (p. 457).

The sulphuric acid salts of the diazo-compounds are particularly well adapted to this end; the nitric acid salts tend to yield nitro-phenols. It is best to dissolve the amido-derivatives in dilute sulphuric acid (2 equivalents), add aqueous potassium nitrite (1 molecule), and boil the strongly diluted solution until the disengagement of nitrogen ceases.

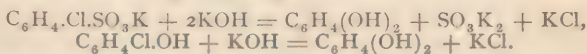
2. Fusion of the sulphonic acids with potassium or sodium hydroxide :—



Here the sulpho-group disappears as a sulphite (p. 120).

The experiment is executed in a silver dish at higher or lower temperatures, the fusion supersaturated with sulphuric acid, and the phenol extracted by shaking with ether.

In fusing sulphonic acids or phenols containing halogens, the latter are also replaced with formation of polyhydric phenols :—



Occasionally the sulpho-group splits off as sulphate and is replaced by hydrogen; thus, cresolsulphonic acid yields cresol.

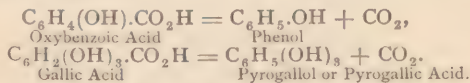
3. Small quantities of phenol are produced from benzene by the action of ozone, hydrogen peroxide (palladium hydride and water), and by shaking with sodium hydroxide and air (*Ber.*, 14, 1144).

4. The halogen benzene substitution products do not react with alkalis; but if nitro-groups are present at the same time, the halogens are replaced even by digesting with aqueous alkalis—this will occur the more readily if the nitro-groups be multiplied. For example, ortho- and para-chloronitro-benzene (but not meta) yield the corresponding nitro-phenols (p. 428), when they are heated to 120° with sodium hydroxide; the dinitro-chlorobenzenes even react when boiled with carbonates, and the trinitro-chlorobenzene even with water.

Nitrophenol-ethers,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{OR}$ , are produced on boiling para-chloronitrobenzene with caustic soda and 60 per cent. alcohol; if absolute alcohol be applied there is simultaneous reduction and formation of chlorazobenzene (*Ber.*, 15, 1005).

The amide-group in the nitroamido-derivatives, can also be replaced by hydroxyl on boiling with aqueous alkalis; ortho- and para-nitranilines,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{NH}_2$  (not meta) yield their corresponding nitrophenols. The ortho-dinitro products react similarly (p. 427).

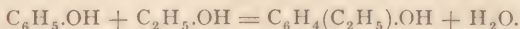
5. The dry distillation of salts of the oxy-acids of the benzene series with lime (p. 412) :—



6. Dry distillation of various complex carbon compounds, *e. g.*,

wood and coal. To isolate the phenol from coal-tar, shake the fraction boiling at  $150-200^{\circ}$ , with aqueous potash, separate the aqueous solution from the oil containing the hydrocarbons, and saturate it with hydrochloric acid. The separated phenols are purified by fractional distillation. Wood-tar oils (*creasote*) consist of a mixture of different phenols and their ethers; the portion, boiling at  $180-300^{\circ}$ , contains phenol,  $C_6H_5.OH$ , para-cresol,  $C_6H_4(CH_3).OH$ , phlorol,  $C_6H_3(CH_3)_2.OH$ , also guaiacol,  $C_6H_4(O.CH_3).OH$ , creosol,  $C_6H_3(CH_3).(O.CH_3).OH$ , and the dimethyl ether of pyrogallol,  $C_6H_3(OH)_3$ , and methyl- and propyl pyrogallol (*Ber.*, **14**, 2005),

7. The synthesis of the higher phenols by introduction of alkyls into the benzene nucleus (p. 412) takes place readily on heating the phenols with alcohols and  $ZnCl_2$  to  $200^{\circ}$  (*Ber.*, **14**, 1842; **17**, 669):—



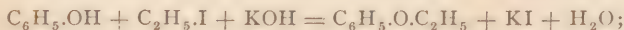
Alkyl ethers of the phenols are simultaneously produced; methyl alcohol affords only methyl-phenol,  $C_6H_5.O.CH_3$ .  $MgCl_2$  (*Ber.*, **16**, 792) and primary alkali sulphates (*Ber.*, **16**, 2541) possess the same condensing power as  $ZnCl_2$ . Phenol and resorcinol condense to ketones, *e.g.*, dioxybenzophenone,  $C_6H_4(OH).CO.C_6H_4.OH$  (*Ber.*, **16**, 2298), when heated with salicylic acid and tin chloride.

8. Many benzene derivatives are transposed in the animal organism into phenols; thus, benzene yields phenol; brombenzene, bromphenol; aniline, amidophenol and phenol hydroquinone. Different phenols are found already formed as phenol-sulphuric acids (p. 482) in the urine of mammals.

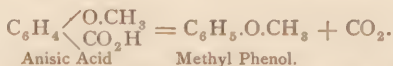
The phenols are the analogues of the tertiary alcohols, but possess a more acidic character (p. 478). The hydrogen of their hydroxyl can be readily substituted by metals, by the action of bases, chiefly of the alkalies. Carbon dioxide separates the phenols again from these salts. The entrance of negative groups into the benzene nucleus increases the acidic nature of the phenols. Thus trinitrophenol manifests the properties of an acid, as it decomposes carbonates.

The hydroxyl-hydrogen of the phenols can also be replaced by alcohol and acid radicals.

The *alcohol-ethers* are formed: by the action of the alkyl iodides upon the salts of the phenols (chiefly the silver salts), or by heating a mixture of the phenols and the alkyl iodides, or alkyl sulphates, with caustic potash (in equivalent quantity) in alcoholic solution:—



and by the dry distillation of the phenol ethers of the oxy-acids with lime:—



Boiling alkalies do not alter the alcohol ethers. When, however,

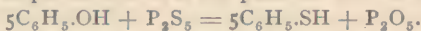
they are heated with hydriodic or hydrochloric acid, they split up into their components:—



The *acid esters* are obtained by acting with acid chlorides or anhydrides upon the phenols or their salts; also by digesting the phenols with acids and  $\text{POCl}_3$ . On boiling with alkalis or even with water, they, like all esters, split into their components.

To effect the substitution of all the hydroxyl-hydrogen atoms in the polyhydric phenols by acetyl groups, it is recommended to heat them with acetic anhydride and sodium acetate.

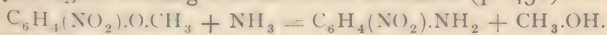
Phosphorus sulphide converts the phenols into thio-phenols:—



The phosphorus haloids replace the hydroxyls of the phenols by halogens, forming substituted benzenes. When heated with zinc dust the phenols are reduced to hydrocarbons. The anilines result on heating with zinc-ammonium chloride (compare p. 432).

On adding phenols (mono- or polyhydric) to a solution of  $\text{KNO}_2$  (6 per cent.) in concentrated sulphuric acid, intense colorations arise; with common phenol we get first a brown, then green, and finally a royal-blue color (Reaction of Liebermann). Dyes are produced in this manner; their character is as yet unexplained. The phenols afford similar colors in presence of  $\text{SO}_4\text{H}_2$  with diazo-compounds, and nitroso-derivatives (p. 459). Ferric chloride imparts colorations to the solutions of most phenols.

The hydrogen of the benzene residue in phenols can be replaced, further, by the halogens and groups  $\text{NO}_2$ ,  $\text{SO}_3\text{H}$ , etc. In the alcohol-ethers of the nitro-phenols (like in the acid esters) we can replace the OH by  $\text{NH}_2$ , on heating with alcoholic ammonia (p. 432):—



The phenols and their halogen products may be converted into oxy-acids by the action of sodium and carbon dioxide (see aromatic series):—



Oxyaldehydes,  $\text{C}_6\text{H}_4(\text{OH}).\text{CHO}$ , are produced from phenols, chloroform and caustic soda and oxyacids (see these) from phenols and carbon tetrachloride. The diazo-yield azo-compounds with phenols—the tropaeoline dyes belong to this class (p. 469). Dyestuffs belonging to the amine series and derived from triphenylmethane,  $\text{CH}(\text{C}_6\text{H}_5)_3$  (see this), are obtained from the phenols in their action on benzotrichloride,  $\text{C}_6\text{H}_5.\text{CCl}_3$ . The so-called phthaleins are combinations of phthalic acid and the phenols.

## MONOVALENT PHENOLS.

Phenol,  $\text{C}_6\text{H}_5.\text{OH}$ .

Cresols,  $\text{C}_6\text{H}_4.\text{CH}_3(\text{OH})$ .

Xylenols,  $\text{C}_6\text{H}_3(\text{CH}_3)_2.\text{OH}$ , etc.

Phenol,  $\text{C}_6\text{H}_5.\text{OH}$  (Benzene Phenol, Carbolic Acid, Creasote). This was first discovered (1834) in coal-tar, by Runge. It is ob-



tained from amidobenzene, from benzene-sulphonic acid, from the three oxy-benzoic acids, etc., by the methods previously described. It occurs already formed in *Castoreum* and in the urine of the herbivoræ.

Commercial phenol is a colorless, crystalline mass, which gradually acquires a reddish color, and deliquesces on exposure to the air. Pure phenol crystallizes in long, colorless prisms, melts at  $42^{\circ}$ , and boils at  $183^{\circ}$ ; its specific gravity at  $0^{\circ}$  is 1.084. It possesses a characteristic odor, burning taste, and poisonous and antiseptic properties. It dissolves in 15 parts water at  $20^{\circ}$ , and very readily in alcohol, ether and glacial acetic acid. Ferric salts impart a violet color to its neutral solutions. Bromine water precipitates tribromphenol from even very dilute solutions. Diphenols,  $C_{12}H_{10}(OH)_2$ , derivatives of diphenyl (see this), are produced on fusing phenol with caustic potash.

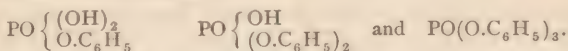
*Potassium Phenylate or Phenoxide*,  $C_6H_5.OK$ , is obtained by dissolving phenol in potassium hydroxide. It crystallizes in delicate, readily soluble needles.  $CO_2$  separates phenol from it, which, therefore, is insoluble in alkaline carbonates. Baryta, lime, and litharge form similar compounds.

*Phenacetin or Phenacetolin*,  $C_{16}H_{12}O_2$  (*Ber.*, 15, 2907), is obtained by heating phenol with acetic acid and  $ZnCl_2$ . This compound is employed as an indicator in alkalimetry (*Ber.*, 15, 2907).

#### PHENOL ACID ESTERS (p. 481)—ETHEREAL SALTS.

*Phenylsulphuric Acid*,  $C_6H_5.O.SO_3H$ , is not known in a free state; when liberated from its salts by concentrated hydrochloric acid, it immediately breaks up into phenol and sulphuric acid. Its *potassium salt*,  $C_6H_5.O.SO_3K$ , forms leaflets, not very soluble in cold water, and occurs in the urine of herbivorous animals, and also in that of man and the dog after the ingestion of phenol. It is synthetically prepared, like other phenols, on heating potassium phenoxide with an aqueous solution of potassium pyrosulphate (*Ber.*, 9, 1715).

The phenol esters of phosphoric acid are produced by the action of  $PCl_5$  upon phenol (together with chlorides):—



The *triphenyl ester* is easily formed on boiling phenol with phosphorus oxychloride (*Ber.*, 16, 1763). It is crystalline, melts at  $45^{\circ}$ , and boils near  $400^{\circ}$ . Distilled with potassium cyanide it yields benzonitrile,  $C_6H_5.CN$ .

The carbonic acid ester, *Phenyl Carbonate*,  $CO(O.C_6H_5)_2$ , is produced on heating phenol and phosgene gas,  $COCl_2$ , to  $150^{\circ}$ . It is readily obtained by leading phosgene gas into the aqueous solution of sodium phenylate (*Journ. pract. Chem.*, 27, 39). It crystallizes from alcohol in shining needles, and melts at  $78^{\circ}$ . It yields sodium salicylate (see this) when heated to  $200^{\circ}$  with sodium phenoxide.

Mixed carbonates containing phenol and alkyls, *e. g.*, phenyl-ethyl carbonate,  $CO_2(C_2H_5)(C_6H_5)$ , are produced by the action of chlor-formic esters upon the sodium salts of the phenols.

The *acetic ester*,  $C_6H_5.O.C_2H_3O$ , is obtained by boiling the phosphoric ester with potassium acetate, and is an agreeably-smelling liquid, boiling at  $190^{\circ}$ .

*Phenyl-glycollic Acid*,  $\text{CH}_2 \begin{smallmatrix} \diagup \text{O.C}_6\text{H}_5 \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$  (isomeric with mandelic acid), is produced by heating monochloroacetic acid with potassium phenate to  $150^\circ$ . Long, silky needles, melting at  $96^\circ$ . All other phenols react analogously.

*Phenyl Ethyl Oxalic Ester*,  $\text{C}_2\text{O}_2 \begin{smallmatrix} \diagup \text{O.C}_6\text{H}_5 \\ \diagdown \text{O.C}_2\text{H}_5 \end{smallmatrix}$ , is formed by the action of chloro-oxalic ester (p. 320) upon phenol, and is an oil boiling at  $236^\circ$ , and is slowly decomposed by water into phenol, oxalic acid and alcohol.

The *succinic ester*,  $\text{C}_2\text{H}_4(\text{CO}_2\cdot\text{C}_6\text{H}_5)_2$ , from phenol and succinyl chloride, forms shining leaflets, melts at  $118^\circ$ , and boils at  $330^\circ$ .

Phenyl-allophanic ester,  $\text{CO} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{NH.CO.C}_6\text{H}_5 \end{smallmatrix}$  (p. 309), is produced by conducting cyanic acid vapors into anhydrous phenol. A crystalline mass, decomposing at  $150^\circ$  into phenol and cyanuric acid.

Phenyl-ortho-formic-ester,  $\text{CH}(\text{O.C}_6\text{H}_5)_3$ , is formed by boiling phenol with sodium hydroxide and chloroform (as a by-product in the formation of oxybenzaldehyde). It crystallizes in white needles, melts at  $71^\circ$  and distils at  $265^\circ$ , under 50 mm. pressure.

#### PHENOL ALCOHOLIC ETHERS (p. 480).

**Methyl Phenyl Ether**,  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_3$ , **Anisol**, is produced by heating phenol with potassium and methyl iodide or potassium methyl sulphate in alcoholic solution; by distilling anisic or methyl salicylic acid with lime or baryta (p. 479); or by leading methyl chloride into sodium phenoxide at  $200^\circ$  (*Ber.*, 16, 2513).

It is an ethereal-smelling liquid, boiling at  $152^\circ$ ; its specific gravity at  $15^\circ$  is 0.991. Heated to  $130^\circ$  with hydriodic acid it splits up into phenol and methyl alcohol. It is not reduced by zinc dust.

Bromine converts it into substitution products; *bromanisol*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{O}\cdot\text{CH}_3$ , boils at  $223^\circ$ ; *dibromanisol* crystallizes in rhombic plates, melts at  $59^\circ$  and boils at  $272^\circ$ ; *tribromanisol* melts at  $87^\circ$  and sublimes. Further action of bromine produces bromanil,  $\text{C}_6\text{H}_3\text{Br}_3\text{O}_2$ .

Nitric acid converts anisol into two *mono-nitroanisols* (1, 4) and (1, 2).

**Ethyl Phenyl Ether** ( $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$ ), **Phenetol**, is obtained from phenol and ethyl salicylic acid. It is an aromatic-smelling ether, boiling at  $172^\circ$ . The isoamyl ether boils at  $225^\circ$ .

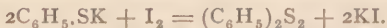
**Ethylene Phenyl Ether** ( $\text{C}_6\text{H}_5\cdot\text{O})_2\cdot\text{C}_2\text{H}_4$ , is formed from ethylene bromide and potassium phenylate. It consists of leaflets, melting at  $95^\circ$ .

**Phenyl Ether** ( $\text{C}_6\text{H}_5)_2\text{O}$ , **Phenyl Oxide**, is produced by distilling copper benzoate (together with benzoic phenyl ether) and digesting diazobenzene sulphate with phenol; also by heating phenol with  $\text{ZnCl}_2$  to  $350^\circ$ , or better, with  $\text{AlCl}_3$  (*Ber.*, 14, 189). It crystallizes in long needles, possesses an odor resembling that of geraniums; melts at  $28^\circ$ , and boils at  $252^\circ$ . It dissolves readily in alcohol and ether. It is not reduced on heating with zinc dust or hydriodic acid.

**Thiophenol**,  $\text{C}_6\text{H}_5\cdot\text{SH}$ , Benzene sulphydrate, is obtained by letting phosphorus pentasulphide act on phenol or sodium benzene sulphonate; or by the action of zinc and sulphuric acid upon  $\text{C}_6\text{H}_5\cdot\text{SO}_2\text{Cl}$  (p. 476). It is a mobile, ill-smelling liquid, boiling at  $168^\circ$ ; its specific gravity at  $14^\circ$  is 1.078. It dissolves readily in alcohol and ether. Like the mercaptans, it reacts readily with metallic oxides. The mercury compound ( $\text{C}_6\text{H}_5\cdot\text{S})_2\text{Hg}$ , crystallizes from alcohol in shining needles. Silver, mercury and lead salts precipitate the alcoholic solution of thiophenol.

**Phenyl Sulphide**,  $(C_6H_5)_2S$ , Benzene sulphide, is formed by distilling phenol with  $P_2S_5$  (along with thiophenol), and in the dry distillation of sodium benzene sulphonate. A colorless liquid with an odor resembling that of leeks; boils at  $292^\circ$ , and has a specific gravity of 1.12.

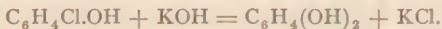
**Phenyl Disulphide**,  $(C_6H_5)_2S_2$ , results from the oxidation of thiophenol with dilute nitric acid, and by the action of iodine upon aqueous potassium thiophenate:—



It crystallizes from alcohol in shining needles, melting at  $60^\circ$ . Nitric acid oxidizes it to benzene sulphonic acid, and nascent hydrogen converts it into thiophenol.

### PHENOL SUBSTITUTION PRODUCTS.

The introduction of halogen atoms considerably increases the acid character of phenol; thus, trichlorophenol readily decomposes the alkaline carbonates. When fused with potassium hydroxide the halogen is replaced by the hydroxyl group (p. 479):—



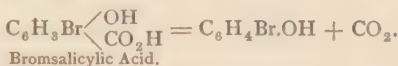
In this reaction it frequently occurs that not the corresponding isomerides, but rather, the more stable derivative, results; for example, all the bromphenols yield resorcinol.

Chlorine and bromine react readily; this is exemplified in bromine precipitating tribromphenol directly upon its introduction into phenol solutions. The iodo-derivatives are formed by adding iodine and iodic acid to a dilute potassium hydroxide solution of phenol:—



or by the action of iodine and mercuric oxide (p. 64). Di-iodophenol is the chief product in the latter case.

Substituted phenols are obtained indirectly: 1, from substituted anilines by the replacement of  $NH_2$  by  $OH$ , which may be brought about through the diazo-compounds; 2, from the nitrophenols by replacing the nitro-group with halogens (effected through the amido- and diazo-derivatives); 3, by distilling substituted oxyacids with lime or baryta:—



Sodium amalgam causes the replacement of the halogen atoms by hydrogen.

**Chlorphenols**,  $C_6H_4Cl.OH$ . The para- and ortho- derivatives are produced by leading chlorine into boiling phenol; they can be separated by fractional distillation. The three chlor- compounds may be obtained perfectly pure from the corresponding chlor anilines (from the chlor-nitro-benzenes). (1, 2)-*Chlorphenol* (also produced from volatile ortho-nitrophenol) boils at  $-176^\circ$ , solidifies at  $-12^\circ$ , and melts at  $+7^\circ$ . It affords pyrocatechin when fused with  $KOH$ . (1, 3)-*Chlorphenol*, from (1, 3)-chlor-aniline, melts at  $28.5^\circ$ , and boils at  $212^\circ$ .

(1, 4)-*Chlorphenol* (para) consists of colorless prisms, which acquire a red color on exposure to the air, melt at  $37^{\circ}$  ( $41^{\circ}$ ) and boil at  $217^{\circ}$ . Hydroquinone is produced when it is fused with caustic potash. The three chlorphenols have a very penetrating, adhering odor.

**Dichlorophenol**,  $C_6H_3Cl_2.OH$ , from phenol (1, 2, 4 — OH in 1), melts at  $43^{\circ}$  and boils at  $210^{\circ}$ . It yields (1, 2, 4)-trichlorophenol with  $PCl_5$ . **Trichlorophenol**,  $C_6H_2Cl_3.OH$  (1, 3, 5, OH) (compare p. 428), obtained by acting on phenol with chlorine, melts at  $68^{\circ}$ , boils at  $244^{\circ}$ , and reacts acid. **Pentachlorophenol**,  $C_6Cl_5.OH$ , formed by the chlorination of phenol in presence of  $SbCl_3$ , melts at  $187^{\circ}$ .

**Bromphenols**,  $C_6H_4Br.OH$ . On conducting bromine vapors into phenols, or in brominating the glacial acetic acid solution of phenol we obtain chiefly (1, 4)- and (1, 2)-monobromphenol; under certain conditions it appears that (1, 3) is also produced. They are obtained pure from the bromanilines.

(1, 2)-*Bromphenol*, from (1, 2)-bromaniline and from (1, 2)-nitrophenol, is a liquid, boiling at  $195^{\circ}$ . (1, 3)-*Bromphenol*, from (1, 3)-bromaniline, melts at  $32-33^{\circ}$ , and boils at  $236^{\circ}$ . (1, 4)-Bromphenol is formed in largest quantity when phenol is treated with bromine, and has also been obtained from (1, 4)-bromaniline and from bromsalicylic acid. It consists of large crystals, melting at  $66^{\circ}$  ( $66.4^{\circ}$ ) and boiling at  $238^{\circ}$ .  $PBr_5$  converts it into (1, 4)-dibrombenzene.

**Dibromphenol**,  $C_6H_3Br_2.OH$  (1, 2, 4 — OH in 1), from phenol, melts at  $40^{\circ}$ . **Tribromphenol**,  $C_6H_2Br_3(OH)$  (1, 3, 5, OH), is directly precipitated from aqueous phenol solutions by bromine water. It crystallizes from alcohol in silky needles, melting at  $92^{\circ}$ .  $PBr_5$  converts it into tetrabrombenzene, melting at  $98^{\circ}$ . Nitric acid converts it into picric acid. **Tetrabromphenol**,  $C_6HBr_4OH$ , melts at  $120^{\circ}$ ; **Pentabromphenol**,  $C_6Br_5OH$ , at  $225^{\circ}$ .

**Iodophenols**,  $C_6H_4I.OH$ . When phenol is acted upon by iodine and iodic acid three mono-iodo-phenols are said to be formed; of these the ortho- and meta- volatilize with steam, the para- does not (*Ber.*, 6, 1251).

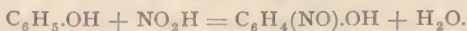
(1, 2)-*Iodophenol* is obtained from (1, 2)-amido-phenol and from iodosalicylic acid. It is also produced when iodine acts upon sodium phenoxide (*Ber.*, 16, 1897). It melts at  $43^{\circ}$  and when fused with KOH yields pyrocatechin (at  $200^{\circ}$ ) and resorcinol. (1, 4 -*Iodophenol*, from phenol, (1, 4)-amidophenol and (1, 4)-iodo aniline, melts at  $89^{\circ}$ , and when fused with KOH affords hydroquinone at  $160^{\circ}$ , but resorcinol at higher temperatures.

#### NITROSO-DERIVATIVES OF PHENOL.

The so-called *nitroso-phenols*,  $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown NO \end{smallmatrix}$ , which, like the nitroso-benzenes (p. 430), are produced by the action of nitrous acid upon the phenols, are, from latest researches, really not nitroso-compounds, but appear to be isonitroso-derivatives (oximido-group  $N.OH$ ), because nitroso-benzenephénol is also formed by the action of hydroxylamine upon quinone, and the two nitrosonaphthols certainly represent isonitroso-compounds (*Ber.*, 17, 213 and 801).

The so-called nitrosophenols are formed:—

1. By the action of nitrous acid upon the phenols:—



Phenol is dissolved in a dilute alkaline hydroxide, the equivalent amount of  $KNO_2$  added, the solution cooled with ice, and gradually supersaturated with dilute sulphuric or acetic acid (*Ber.*, 8, 614).



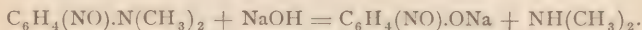
2. By the action of nitro-sulphuric acid,  $\text{SO}_2 \begin{smallmatrix} \diagup \text{O.NO} \\ \diagdown \text{OH} \end{smallmatrix}$ , upon aqueous phenols (*Ann.*, 188, 353).

In both reactions nitrous acid is liberated and occasions the production of considerable resin. Hence, it is advisable to employ the nitrites of heavy metals, which are decomposed by the phenols themselves (*Ber.*, 16, 3080).

3. By the action of amyl nitrite upon sodium phenoxides.

It is noteworthy that while the monovalent phenols yield only mono-nitroso-compounds, two nitroso-groups directly enter the divalent phenols (like resorcinol and orcinol).

**Para-Nitrosophenol**,  $\text{C}_6\text{H}_4(\text{NO}).\text{OH}$  (?). Besides the general methods just mentioned, it is also obtained by a peculiar decomposition of nitroso-dimethyl- or diethyl aniline (p. 438) with sodium hydroxide:—



It is produced, further, by the action of hydroxylamine hydrochloride upon an aqueous solution of quinone,  $\text{C}_6\text{H}_4\text{O}_2$  (see above).

*Preparation.*—It is made from phenol by the action of  $\text{NO}_2\text{K}$  and acetic acid (*Ber.*, 7, 967), or nitroso-sulphuric acid (*Ann.*, 188, 360). Its production from nitroso-dimethyl-aniline is more convenient. The pure (free of alcohol) hydrochloride of the latter is introduced into boiling, dilute sodium hydroxide, the dimethyl-amine formed is distilled off, the residue acidified with dilute sulphuric acid, and then shaken with ether (*Ber.*, 7, 964, and 8, 622).

We can easily obtain sodium nitrosophenylate by adding phenol (1 molecule), and then amyl nitrite (1 molecule) to a concentrated solution of sodium ethylate (1 molecule), and allowing the whole to evaporate over sulphuric acid (*Ber.*, 17, 400).

The free nitrosophenol is obtained by decomposing the sodium salt with dilute sulphuric acid (*Ber.*, 17, 803).

Pure nitrosophenol crystallizes from hot water in colorless, delicate needles, which readily brown on exposure, and from ether it separates in large, greenish-brown leaflets. It is soluble in water, alcohol and ether, and imparts to them a bright green color. When heated it melts with decomposition, and deflagrates at  $110-120^\circ$ . The sodium salt crystallizes in red needles, containing  $2\text{H}_2\text{O}$ ; salts of the heavy metals throw out dark, amorphous precipitates.

Nitric acid, and also potassium ferricyanide in alkaline solution, oxidizes nitrosophenol to para-nitrophenol. Tin and hydrochloric acid reduce it to para-amidophenol. Hydrochloric acid converts it into dichloramidophenol. With nitrous acid and with hydroxylamine, it yields diazo-phenol:—



In a similar manner it affords azo-compounds with the amines (p. 463); these are obtained, too, on fusion with caustic alkali. On adding a little concentrated sulphuric acid to a mixture of nitrosophenol and phenol, we obtain a dark red coloration, which changes to dark blue upon adding caustic potash (p. 481).

Other phenols, like naphthol, resorcinol and orcinol, yield similar nitroso-derivatives.

## NITRO-PRODUCTS OF PHENOL.

The phenols, like the anilines, are very readily nitrated. The entrance of the nitro-groups increases their acidic character very considerably. All nitrophenols decompose alkaline carbonates. Trinitrophenol is a perfect acid in its behavior; its chloranhydride,  $C_6H_2(NO_2)_3Cl$ , reacts quite readily with water, re-forming trinitrophenol (p. 481). The benzene nucleus of the nitrophenols is capable of ready substitution with the halogens; whereas the nitro-hydrocarbons are chlorinated with difficulty.

Dilute nitric acid converts phenol into ortho- and para-mono-nitrophenol (in the cold it is chiefly the para-compound which is formed).

*Preparation.*—Gradually add one part phenol to a cooled solution of two parts nitric acid (specific gravity 1.34) in four parts water. The oil which separates is washed with water and distilled with steam, when the volatile (1, 2)-nitrophenol distils over, while the non-volatile (1, 4)-nitrophenol remains. It is extracted from the residue by boiling with water.

Ortho- and para-nitrophenols are obtained by heating the corresponding chlor- and brom-nitrobenzenes with caustic potash to  $120^\circ$ , whereas metabrom-nitrobenzene does not react under similar circumstances (p. 428). Ortho- and para-nitrophenols are likewise produced from the corresponding nitranilines by heating with alkalis (p. 481). m-Nitrophenol is formed from m-nitraniline (from ordinary dinitrobenzene) by boiling the diazo-compound with water.

**Mononitrophenols**,  $C_6H_4OH(NO_2)$ . The volatile *orthonitrophenol* (1, 2) crystallizes in large yellow prisms, is but slightly soluble in water, and readily volatilizes with steam. It has a peculiar odor, and sweetish taste; melts at  $45^\circ$ , and boils at  $214^\circ$ . (1, 2)-Chlornitro-benzene is obtained from it by  $PCl_5$ . Its sodium salt is anhydrous, and forms dark red prisms. The methyl ether,  $C_6H_4(NO_2).O.CH_3$ , melts at  $+9^\circ$ , and boils at  $265^\circ$ . Caustic potash does not decompose it.

(1, 3)-*Nitrophenol*, from (1, 3)-nitraniline, is rather readily soluble in cold water, forms yellow crystals, melts at  $96^\circ$ , and is not volatilized with steam. Its methyl ether melts at  $38^\circ$ , and boils at  $254^\circ$ .

(1, 4)-*Nitrophenol* crystallizes from hot water in long, colorless needles, which become red on exposure. It is odorless and melts at  $114^\circ$ .  $PCl_5$  converts it into (1, 4)-chlornitrobenzene. The potassium salt crystallizes in yellow needles with  $2H_2O$ . The methyl ether melts at  $48^\circ$ , and boils at  $260^\circ$ ; it forms (1, 4)-nitraniline when heated with ammonia. Nitrophenol can, on the one hand, be changed to quinone, on the other, into anisic acid.

Bromine converts para-nitrophenol into dibrom-para-nitrophenol,  $C_6H_2Br_2\begin{smallmatrix} NO_2 \\ \diagup \diagdown \\ OH \end{smallmatrix}$  (1, 4, 2, 6), melting at  $141^\circ$ . This yields **Dibrom-para-amidophenol**, when reduced with tin and hydrochloric acid. The latter (its  $SnCl_4$ -salt) is converted by bleaching lime into dibrom-quinone-chlorimide,  $C_6H_2Br_2\begin{smallmatrix} NCl \\ | \\ O \end{smallmatrix}$ ,

which yields indophenol dyestuffs (see quinone chlorimides) with phenols.

**$\alpha$ -Dinitrophenol**,  $C_6H_3(NO_2)_2.OH$  (1, 2, 4—OH in 1), is formed by the direct nitration of phenol, as well as of (1, 2)- and (1, 4)-nitrophenol; by boiling

$\alpha$ -dinitro-chlor- and dinitro-brom-benzene (p. 429) with alkalis, and (together with  $\beta$ -dinitrophenol) by oxidizing metadinitrobenzene with alkaline potassium ferricyanide. It crystallizes from alcohol in yellow plates, and melts at  $114^{\circ}$ .  $\text{PCl}_5$  changes it to dinitrochlorbenzene. Its methyl ether melts at  $86^{\circ}$ , and is saponified by boiling alkalis. The ether is transformed into  $\alpha$ -dinitraniline by heating with ammonia. From this (1, 3)-dinitrobenzene may be prepared by replacing the amido group by hydrogen (through the diazo-compound).

$\beta$ -Dinitrophenol (1, 2, 6—OH in 1) is produced with the former in the nitration of (1, 2)-nitrophenol. It yields needles melting at  $64^{\circ}$ . By replacing its OH-group with hydrogen it passes into (1, 3)-dinitrobenzene.

Further nitration converts both dinitrophenols into picric acid. Three isomeric dinitrophenols are obtained by the nitration of (1, 3)-nitrophenol; these melt at  $104^{\circ}$ ,  $134^{\circ}$  and  $141^{\circ}$ . Further action of nitric acid converts them into trinitroresorcinol.

**Trinitrophenols,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$ . Picric Acid** is obtained by the nitration of phenol, of (1, 2)- and (1, 4)-nitrophenol, and of the two dinitrophenols; also by the oxidation of symmetrical trinitrobenzene with potassium ferricyanide. Its structure is therefore 1, 2, 4, 6 (OH in 1) (p. 428).

Picric acid is produced in the action of concentrated nitric acid upon various organic substances, like indigo, aniline, resins, silk, leather and wool.

*Preparation.*—Add phenol (1 part) very gradually to concentrated nitric acid, slightly warmed. The reaction proceeds with much energy, and disengages brown vapors. Next add three parts fuming nitric acid and boil for some time, until the evolution of vapors ceases. The resulting resinous mass is boiled with hot water. To purify the picric acid obtained, convert the latter into its sodium salt, and to its solution add sodium carbonate when sodium picrate will separate in a crystalline form.

Picric acid crystallizes from hot water and alcohol in yellow leaflets or prisms which possess a very bitter taste. It dissolves in 160 parts cold water and rather readily in hot water. Its solution imparts a beautiful yellow color to silk and wool. It melts at  $122.5^{\circ}$  and sublimes undecomposed when carefully heated. The *potassium salt*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK}$ , crystallizes in yellow needles, which dissolve in 260 parts water at  $15^{\circ}$ . The sodium salt is soluble in 10 parts water at  $16^{\circ}$ , and is separated from its solution by sodium carbonate. The ammonium salt consists of beautiful, large needles, and is applied in explosive mixtures. All the picrates explode very violently when heated or struck.

$\text{PCl}_5$  converts picric acid into trinitro-chlor-benzene,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{Cl}$  (p. 429), which reverts to picric acid on boiling with water.

The *methyl ester* of picric acid is also produced in the nitration of anisol (p. 483) and crystallizes in plates, melting at  $65^{\circ}$ , and subliming. Alcoholic potash saponifies it. The *ethyl ester* consists of colorless needles, which brown on exposure, and melt at  $78.5^{\circ}$ .

Picric acid affords beautiful crystalline derivatives with many benzene hydrocarbons, *e. g.*, benzene, naphthalene and anthracene. The *benzene derivative*,

$C_6H_2(NO_2)_3OH \cdot C_6H_5$ , crystallizes in needles, melting at  $85-90^\circ$ . In dry air or with hot water it decomposes into its components.

The so-called isopicric acid, obtained by the energetic nitration of (1, 3)-nitrophenol, is trinitroresorcinol,  $C_6H(NO_2)_3 \cdot (OH)_2$  (styphnic acid).

Picric acid is converted by potassium cyanide into the potassium salt of *isopurpuric* or *picrocyaminic acid*,  $C_8H_5N_5O_6$ , which is not stable in a free state. To obtain the salt the hot solution of 1 part picric acid in 9 parts water is poured gradually into a solution of 2 parts CNK in 4 parts of water, at a temperature of  $60^\circ$ . The liquid assumes a dark red color, and when it cools a crystalline mass separates, which is washed with cold water and crystallized from hot water.

The potassium salt,  $C_8H_4N_5O_6K$ , crystallizes in brown leaflets with green-gold lustre, and serves as a substitute for *archil*. It dissolves in hot water and alcohol with a purple-red color. It explodes at  $215^\circ$ . The other salts of isopurpuric acid are obtained by double decomposition.

The dinitrophenols afford similar derivatives with CNK.

Two isomeric **Trinitrophenols** ( $\beta$ - and  $\gamma$ -) are obtained by nitrating the dinitrophenols prepared from meta-nitrophenol and are very similar to picric acid.  $\beta$ -Trinitrophenol melts at  $96^\circ$ ;  $\gamma$ -trinitrophenol at  $117^\circ$  (*Ber.*, 16, 235).

Innumerable chlornitrophenols have been obtained by the action of the halogens upon the nitrophenols, or by nitration of the halogen derivatives.

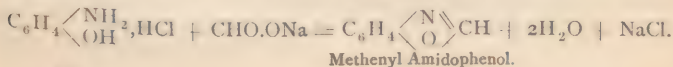
## AMIDO-DERIVATIVES OF PHENOL.

These, like the anilines, are obtained by the reduction of the nitrophenols. In the case of the poly-nitrated phenols, ammonium sulphide occasions but a partial, tin and hydrochloric acid, however, a complete, reduction of the nitro-groups (p. 431). Thus, dinitrophenol,  $C_6H_3(NO_2)_2 \cdot OH$ , yields nitro-amido-phenol,  $C_6H_3(NO_2)(NH_2) \cdot OH$ , and diamido-phenol,  $C_6H_3(NH_2)_2 \cdot OH$ .

The amido-group considerably diminishes the acid character of the phenols. This class of derivatives no longer affords salts with alkalies, and only yields such compounds with the acids. Their amido-hydrogen, like that of the anilines, is replaced by acid radicals on heating with acid chlorides or anhydrides. The products of the ortho-series readily part with water and pass (like the orthodiamido-compounds) into *anhydro-bases* (p. 455):—



The corresponding methenyl compounds are easily formed by distilling the HCl-amido-phenols with sodium formate (*Ber.*, 14, 570):—





Amidophenols are regenerated on heating the ethenyl compounds with hydrochloric acid.

The amidothiophenols of the ortho-series afford perfectly analogous anhydro-derivatives (p. 491).

### Monoamidophenols, $C_6H_4(NH_2).OH$ .

Ortho-amidophenol is produced from orthonitrophenol by reduction with tin and hydrochloric acid, and is precipitated from its HCl-salt in colorless leaflets, which rapidly turn brown. It is more easily obtained by dissolving ortho-nitrophenol in alcoholic ammonia, and leading  $H_2S$  into the solution, when the phenol separates in crystalline form. It melts at  $170^\circ$ , and is difficultly soluble in water (in 50 parts). **Methenyl Amidophenol**, Carbamido-phenol,  $C_7H_5NO$  (see above), melts at  $30^\circ$ , and boils at  $182^\circ$ . The ethenyl compound is a liquid, and

boils at  $182^\circ$ . **Benzenyl-amidophenol**,  $C_6H_4 \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C_6H_5$ , is produced by the reduction of benzoyl-ortho-nitrophenol, and when digested with hydrochloric acid yields **Benzoyl-amido-phenol**,  $C_6H_4(OH).NH.CO.C_6H_5$ . All the acid esters of ortho-nitrophenol (*Ber.*, 16, 1933) deport themselves similarly.

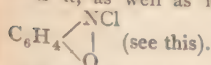
**Oxyphenyl-urea**,  $C_6H_4(OH).NH.CO.NH_2$ , formed by the action of potassium cyanate upon HCl-ortho-amido-phenol, melts at  $154^\circ$ . It forms **Oxyphenylthiurea**,  $C_6H_4(OH).NH.CS.NH_2$ , with potassium thiocyanate. This melts at  $161^\circ$ .

**Oxy-carbamido-phenol**,  $C_6H_4 \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C.OH$ , Oxy-methenyl-amidophenol, is obtained by the action of chlorcarbonic esters upon ortho-amido-phenol, when a condensation takes place. It is produced, too, on heating oxyphenyl urea (with splitting-off of  $NH_3$ ) (*Ber.*, 16, 1828). It sublimes in pearly leaflets, melts at  $137^\circ$ , and yields an acetyl derivative which melts at  $137^\circ$ . **Thiohydriyl-carbamido-phenol**,  $C_6H_4 \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C.SH$ , is produced by the action of  $CS_2$  upon ortho-amido-phenol, or of potassium xanthate upon the HCl-salt; also by heating oxyphenyl urea (see above) (*Ber.*, 16, 1825). It melts at  $193$ – $196^\circ$ , and dissolves in alkalis and ammonia. It forms **Anilido-carbamidophenol**,  $C_6H_4 \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C.NH.C_6H_5$  (with elimination of  $NH_3$ ), which melts at  $173^\circ$ . **Amido-carbamido-phenol**,  $C_6H_4 \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C.NH_2$  (called phenylene urea), results on desulphurizing oxyphenylthiurea by boiling it with  $HgO$  and alcohol. It dissolves readily in water and ether, crystallizes in large plates, and melts at  $130^\circ$ .

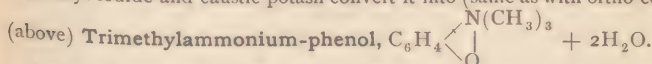
Methyl iodide (3 molecules) and potassium hydroxide change ortho-amido-phenol (analogous to the formation of betaine from glycocoll, p. 293) into **Trimethyl ammoniumphenol**,  $C_6H_4 \begin{smallmatrix} \diagup N(CH_3)_3 \\ \diagdown O \end{smallmatrix}$ , which crystallizes from water in white prisms, containing  $1H_2O$ . It tastes bitter, and dissolves easily in water but not in ether. Its HCl-salt,  $C_6H_4 \begin{smallmatrix} \diagup N(CH_3)_3Cl \\ \diagdown OH \end{smallmatrix}$ , gives the base again with silver oxide; it breaks up by distillation into  $CH_3Cl$  and **Dimethyl-amido-phenol**,  $C_6H_4(OH).N(CH_3)_2$ , which melts at  $45^\circ$  (*Ber.*, 13, 246). The cumazonic acids (see these) possess a constitution analogous to that of the condensation products of ortho-amido-phenol.

**Meta-amidophenol**,  $C_6H_4(NH_2).OH$  (1, 3), is obtained by the reduction of meta-nitrophenol with tin and hydrochloric acid. It is very readily decomposed, and yields resorcin with nitrous acid.

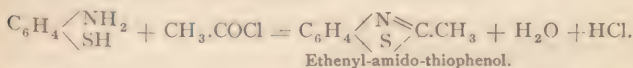
*Para-amidophenol*,  $C_6H_4(NH_2).OH$ , is obtained by reducing para-nitrophenol with tin and hydrochloric acid, and by distilling amidosalicylic acid. It sublimes in shining leaflets, and melts at  $184^\circ$  with decomposition. It is oxidized to quinone by chromic acid, or by  $PbO_2$  and sulphuric acid. Bleaching lime converts it, as well as its substitution products, into quinone chlorimides, *e. g.*,



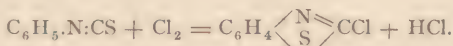
Methyl iodide and caustic potash convert it into (same as with ortho-compound)



**Amido-thiophenol**,  $C_6H_4(NH_2)SH$  (1, 2), is obtained from ortho-nitro-benzene-sulphonic chloride,  $C_6H_4(NO_2).SO_2Cl$ , by reduction with tin and hydrochloric acid; also from acetanilide,  $C_6H_5.NH.CO.CH_3$ , by heating with sulphur and fusing with caustic alkali (*Ber.*, 13, 1226). It crystallizes in needles; melting at  $26^\circ$ , and boiling at  $234^\circ$ . *Thioanhydro-derivatives* result if it be heated with chlorides or anhydrides of the acids (same as from the ortho-amidophenols—see above):—



They split up into their components when fused with alkalis. The **Methenyl** compound,  $C_6H_4 \begin{array}{c} \diagup N \\ | \\ \diagdown S \end{array} CH$  (isomeric with phenyl mustard oil,  $C_6H_5.N:CS$ , and phenyl sulphocyanate,  $C_6H_5.S.CN$ ), is produced on heating amidothiophenol with formic acid. It is an oil smelling like pyridine, and boiling at  $230^\circ$ . It is also produced by the action of tin and hydrochloric acid on the chloride (chlorphenyl mustard-oil), which results from phenyl mustard-oil on heating it to  $160^\circ$  with  $PCl_5$ :—

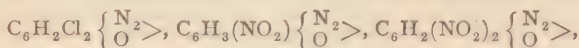


**Chlormethenyl-amido-thiophenol**,  $C_6H_4NSCl$ , melts at  $24^\circ$ , and boils at  $248^\circ$ . The chlorine atom in it is readily adapted to double decompositions (*Ber.*, 13, 8). The *hydroxide*,  $C_6H_4(SN)C.OH$ , melts at  $136^\circ$ , and the *amide*,  $C_6H_4(SN)C.NH_2$ , at  $129^\circ$  (*Ber.*, 16, 1830).

**Dinitro-amido-phenol**,  $C_6H_2(NH_2).(NO_2)_2.OH$ , *picramic acid*, is obtained by reducing ammonium picrate in alcoholic solution with hydrogen sulphide. It forms red needles, which melt at  $165^\circ$ . It yields red-colored crystalline salts with bases.

**Triamidophenol**,  $C_6H_2(NH_2)_3.OH$ , is obtained from picric acid by the action of phosphorus iodide, or by tin and hydrochloric acid (*Ber.*, 16, 2400). When set free from its salts it decomposes very quickly. Its salts, with 3 equivalents of acids, crystallize well. The III-salt,  $C_6H_3O(NH_2)_3.3HI$ , crystallizes in colorless needles. These salts color water which is faintly alkaline, and even spring water, a beautiful blue. If ferric chloride be added to the solution of the hydrochloride, it will become deep blue in color, and brown-blue needles with metallic lustre will separate; they are *HCl-amido-di-imido-phenol*,  $C_6H_2(OH)(NH_2) \begin{array}{c} \diagup NH \\ | \\ \diagdown NH \end{array}$ , which dissolves in water with a beautiful blue color.

*Diazo-compounds of the Phenols.* Their salts result by the action of nitrous acid upon the amido-phenols; free diazo-compounds have been obtained from the substituted amido-phenols, *e. g.*:—



in which the second affinity of the diazo-group appears to be joined to oxygen (p. 456).

The *azo-derivatives* of the phenols are produced by reduction of the nitro-phenols in alcoholic potassium hydroxide solution (p. 439); by the fusion of the nitrophenols (and of nitrosophenol) with caustic potash (*Ber.*, 11, 389), further, by the action of the anilines on the nitrosophenols. They are perfectly analogous to the *azo-derivatives* of the benzenes (*Ber.*, 17, 272).

### PHENOL-SULPHONIC ACIDS.

**Ortho- and Para-phenolsulphonic Acid** are formed when phenol dissolves in concentrated sulphuric acid; at medium temperatures the former is the more abundant, but readily passes into the *para*- on the application of heat.

To obtain the acids, the solution of phenol in sulphuric acid (equal parts) is diluted with water and saturated with calcium carbonate. The filtrate from the gypsum, containing the calcium salts, is boiled with potassium carbonate, thus producing potassium salts. On allowing it to crystallize the potassium salt,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{SO}_3\text{K}$ , of the *para*-acid first separates in hexagonal plates; later the ortho-salt,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{SO}_3\text{K} + 2\text{H}_2\text{O}$ , crystallizes out in prisms, which soon effloresce on exposure (*Ann.*, 205, 64).

The free acids can be obtained in crystalline form by the slow evaporation of the aqueous solution. When the aqueous ortho-acid is boiled it changes to para. The para-acid yields quinone if its sodium salt be oxidized with  $\text{MnO}_2$  and sulphuric acid.  $\text{PCl}_5$  converts it into (1, 4)-chlor-phenol and (1, 4)-dichlorbenzene. When the ortho-acid is fused with  $\text{KOH}$  at  $310^\circ$  it yields pyrocatechin—hence it belongs to the ortho-series; the para-acid does not react at  $320^\circ$ , and at higher temperatures affords diphenols.

**Meta-phenolsulphonic Acid** (1, 3) is produced when meta-benzene-disulphonic acid (p. 476) is heated to  $170$ – $180^\circ$  with aqueous potassium hydroxide (*Ber.*, 9, 969). The potassium salt,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{SO}_3\text{K} + \text{H}_2\text{O}$ , effloresces in the air; the free acid consists of delicate needles, and contains 2 molecules of  $\text{H}_2\text{O}$ . Fusion with potassium hydrate at  $250^\circ$  converts it into resorcinol (1, 3). When para-benzene-disulphonic acid is heated with caustic alkali, meta-phenolsulphonic acid is also produced at first, but it yields resorcinol later.

**Phenol-disulphonic Acid**,  $\text{C}_6\text{H}_3(\text{OH})\cdot(\text{SO}_3\text{H})_2$ , results from the action of an excess of sulphuric acid upon phenol, also upon (1, 2)- and (1, 4)-phenol-sulphonic acid, hence its structure is (1, 2, 4—OH in 1). It is further produced in the action of  $\text{SO}_3\text{H}_2$  upon diazobenzene sulphate. The solution of the acid and its salts is colored a dark red by ferric chloride.

**Phenol-trisulphonic Acid**,  $\text{C}_6\text{H}_2(\text{OH})\cdot(\text{SO}_3\text{H})_3$  (1, 3, 5, OH), is obtained when concentrated sulphuric acid and  $\text{P}_2\text{O}_5$  act upon phenol. It crystallizes in thick prisms with  $3\frac{1}{2}\text{H}_2\text{O}$ .

## HOMOLOGOUS PHENOLS.

**Cresols**,  $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown OH \end{smallmatrix}$ , Oxy-toluenes.

The cresol contained in coal-tar appears to contain three isomerides, but they cannot be separated. They are obtained pure from the amido-toluenes (toluidines) by replacing the group  $NH_2$  by  $OH$ , and from the toluene-sulphonic acids by fusion with potassium hydroxide. The cresols are changed to toluene when heated with zinc dust.  $Na$  and  $CO_2$  produce the corresponding cresotinic acids.

*Ortho-cresol* (1, 2), from ortho-toluidine and ortho-toluene-sulphonic acid, melts at  $31^\circ$ , and boils at  $188^\circ$ . It is obtained from carvacrol (p. 495) when heated with  $P_2O_5$ . It yields salicylic acid (1, 2) on fusion with  $KOH$ ;  $Fe_2Cl_6$  colors it blue. For its nitro-derivatives, see *Ber.*, 15, 1860, and 17, 270.

*Nitroso-o-cresol* melts at  $134^\circ$ . Consult *Ber.*, 17, 351, for azo- and diazo-compounds of the cresols.

*Meta-cresol* (1, 3) is formed from thymol (p. 494), when digested with phosphoric anhydride:—



A cresol-phosphoric-ester is first produced and then saponified by caustic potash. Meta-cresol is a thick liquid, which does not solidify at  $-80^\circ$ , and boils at  $201^\circ$ . Its benzoyl derivative,  $C_7H_7O.C_7H_5O$ , melts at  $38^\circ$ , and boils at  $300^\circ$ . The methyl ether is an oil boiling at  $176^\circ$ ; it is oxidized by potassium permanganate to methyl-meta-oxybenzoic acid. Meta-cresol yields meta-oxy-benzoic acid on fusion with  $KOH$ . Consult *Ber.*, 15, 1130 and 1864, upon nitrometa-cresols.

*Para-cresol* (1, 4), from solid paratoluidine, and from para-toluenesulphonic acid, forms colorless needles, melting at  $36^\circ$ , and boiling at  $198^\circ$ . Its odor resembles that of phenol, and it is difficultly soluble in water. Ferric chloride imparts a blue color to the aqueous solution. It yields paraoxybenzoic acid when fused with  $KOH$ . The benzoyl compound,  $C_7H_7O.C_7H_5O$ , crystallizes in six-sided plates, and melts at  $70^\circ$ . The ethyl ether,  $C_7H_7O.C_2H_5$ , is an aromatic-smelling liquid, which boils at  $188^\circ$ . The methyl ether boils at  $174^\circ$ . Chromic acid oxidizes it to anisic acid,  $C_6H_4(O.CH_3).CO_2H$ .

The nitration of para-cresol produces different nitro-cresols. *Dinitro-cresol*,  $C_7H_5(NO_2)_2OH$  (1, 4, 2, 6), is also obtained by the action of nitrous acid upon paratoluidine (*Ber.*, 15, 1859), and as potassium or ammonium salt represents commercial *Victoria orange* or *Gold-yellow*. It consists of yellow crystals, melting at  $84^\circ$ , and is more difficultly soluble in water than picric acid. Mixed with indigo-carmin it forms *emerald green* (for liqueurs), and with aniline a *carmine surrogate*.

Commercial *Saffran-surrogate* is a mixture of the potassium salts of dinitro-para- and ortho-cresols.

**Thio-cresols**,  $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown SH \end{smallmatrix}$ , Toluene sulphydrates, are obtained by the reduction of the chlorides of the three toluene sulphonic acids with zinc and hydrochloric acid (p. 474). (1, 2)-Thiocresol melts at  $15^\circ$ , and boils at  $188^\circ$ . (1, 3)-Thiocresol is a liquid, and does not solidify at  $-10^\circ$ . (1, 4)-Thiocresol crystallizes in large leaves, melts at  $43^\circ$ , and boils at  $188^\circ$ .

It is singular that the cresols, and all other higher phenols, cannot be oxidized with a chromic acid mixture; *the OH-group prevents the oxidation of the alkyl group*. If, however, the phenol



hydrogen be replaced by alkyls or by the acetyl group (in the phenol ethers and esters), the alkyl is oxidized and oxyacids (their ether acids) produced :—



Potassium permanganate completely destroys the homologous phenols (with free hydroxyls).

The oxidation of the alkyls in the sulphonic acids of the homologous benzenes is dependent upon the position of the sulpho-group. In general, *negative atoms, or atomic groups, prevent the oxidation of the alkyls in the ortho-position by acid oxidizing agents* (pp. 424 and 429), whereas alkaline oxidizers (like  $\text{MnO}_4\text{K}$ ) do the reverse, that is, first oxidize the alkyl occupying the ortho-position (*Ann.*, 220, 16).

Consult *Ber.*, 14, 687, on the department of cresols in the animal organism.

**Phenols,  $\text{C}_6\text{H}_9\text{OH}$ .**

Four xylenols,  $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{OH}$ , have been prepared by fusing isomeric xylene-sulphonic acids with potassium hydroxide. Further fusion oxidizes them to oxy-toluic and oxyphthalic acids. So-called *Phlorol*, from the tar of beech wood boiling near  $220^\circ$ , is also a xyenol. Oxyphthalic acid is produced when its methyl ether (boiling near  $200^\circ$ ) is oxidized.

*Ethyl Phenol*,  $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)\text{OH}$ , from  $\alpha$ -ethylbenzene sulphonic acid, melts at  $47^\circ$ , and boils at  $214^\circ$ . Digested with  $\text{P}_2\text{O}_5$  it splits up into ethylene and phenol-phosphoric acid. An *isomeric ethyl phenol*, called *phlorol*, is obtained by the distillation of barium phloretnate; it is liquid and boils at  $220^\circ$ .

**Phenols,  $\text{C}_9\text{H}_{11}\text{OH}$ .**

*Mesitylol*,  $\text{C}_6\text{H}_2(\text{CH}_3)_3\text{OH}$ , from amido-mesitylene and mesitylene sulphonic acid, is crystalline, melts at  $68-69^\circ$ , and boils at  $220^\circ$ . Isomeric *Pseudocumenol*,  $\text{C}_6\text{H}_2(\text{CH}_3)_3\text{OH}$ , from pseudo-cumene-sulphonic acid, consists of delicate needles, melting at  $69^\circ$ , and boiling at  $240^\circ$ . If fused with  $\text{KOH}$ , it forms oxyxylic acid.

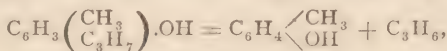
*Propyl Phenol*,  $\text{C}_6\text{H}_4(\text{OH})\text{C}_3\text{H}_7$ , from amido-propyl benzene, boils at  $227^\circ$ . Para-isopropyl-benzene,  $\text{C}_6\text{H}_4(\text{C}_3\text{H}_7)\text{OH}$ , from isopropyl-benzenesulphonic acid, melts at  $61^\circ$ , and boils at  $229^\circ$ .

**Phenols,  $\text{C}_{10}\text{H}_{13}\text{OH}$ .**

Of the innumerable possible isomerides with this formula, Thymol and Carvacrol merit notice. They occur in vegetable oils. Both are methyl-propyl-phenols :—



and are derived from ordinary para-cymene (p. 419). In thymol the OH-group is in the meta-position with reference to the methyl group; in carvacrol, however, in the ortho-position. Both decompose into propylenes and cresols when heated with  $\text{P}_2\text{O}_5$  :—



thymol yielding meta-cresol and carvacrol para-cresol.

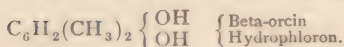
Thymol exists with cymene,  $\text{C}_{10}\text{H}_{14}$ , and thymene,  $\text{C}_{10}\text{H}_{16}$ , in oil of thyme (from *Thymus serpyllum*), and in the oils of *Ptychotis*

*ajowan* and *Monarda punctata*. To obtain the thymol shake these oils with potassium hydrate, and from the filtered solution precipitate thymol with hydrochloric acid. It is artificially prepared from nitrocuminaldehyde,  $C_6H_3(NO_2).(C_3H_7).CHO$ , by the action of  $PCl_5$ , and the reduction of the resulting dichloride (*Ber.*, 15, 166). It crystallizes in large colorless plates, melting at  $44^\circ$  ( $50^\circ$ ), and boiling at  $230^\circ$ . It readily affords a *nitroso*-compound with nitrous acid; this melts at  $161^\circ$ .

So-called **Carvacrol**, Oxycymene, is obtained from cymenesulphonic acid by fusion with KOH, and by heating camphor with iodine ( $\frac{1}{5}$  part) or  $ZnCl_2$ . It is further produced on warming isomeric carvol,  $C_{10}H_{14}O$ , contained in cumen oil (*Carum carvi*) and various other oils, with phosphoric acid. It is a thick oil, solidifying at  $-20^\circ$ ; it melts at  $0^\circ$ , and boils at  $236^\circ$ . Distilled with  $P_2S_5$ , it yields cymene and *thiocymene*,  $C_{10}H_{14}S$ , which boils at  $235^\circ$ .

**Isobutyl Phenol**,  $C_6H_4(C_4H_9).OH$ , and **Amyl Phenol**,  $C_6H_4(C_5H_{11}).OH$ , are readily obtained by heating phenol with isobutyl, and amyl alcohol in presence of  $ZnCl_2$  (p. 480). The former has also been prepared from isobutyl-aniline,  $C_6H_4(C_4H_9).NH_2$ , melts at  $99^\circ$ , and boils at  $231^\circ$ ; the latter melts at  $92^\circ$ , and boils at  $249^\circ$ .

### DIVALENT (DIHYDRIC) PHENOLS.

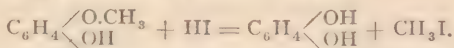


These are obtained, like the monovalent phenols, by fusing monohalogen phenols,  $C_6H_4X.OH$ , halogen benzenesulphonic acids and phenolsulphonic acids with potassium hydroxide (p. 479). It must, however, be observed that often the corresponding dioxybenzenes do not result, but in their stead (especially at higher temperatures) the more stable resorcinol (1, 3). They are also produced by diazotizing the amidophenols, and by the dry distillation of aromatic dioxyacids with lime or baryta.

The dioxybenzenes belonging to the para-series are capable of forming quinones,  $C_6H_4O_2$ , when oxidized.

**Pyrocatechin**,  $C_6H_4(OH)_2$  (1, 2), Oxyphenic Acid, Catechol, was first obtained in the distillation of catechine (the juice of *Mimosa catechu*). It is formed by the dry distillation of proto-catechuic acid,  $C_6H_3(OH)_2.CO_2H$ , of catechuic and Moringa tannic acids, and from (1, 2)-chlor- and iodo-phenols, or (1, 2)-phenolsulphonic acid and many resins on fusion with potassium hydroxide.

It is best prepared by heating guaiacol (from that portion of beech-wood tar boiling at 195–205°) to 200° with hydriodic acid :—



Or, ortho-phenolsulphonic acid may be fused with caustic alkalis (8 parts) to 330–360° (*Journ. pract. Chem.*, 20, 308).

Pyrocatechin crystallizes from its solutions in short, rhombic prisms, and sublimes in shining leaflets. It is soluble in water, alcohol and ether. It melts at 104°, and boils at 245°. On exposure to the air its alkaline solutions assume a green, then brown and finally a black color. Lead acetate throws out a white precipitate,  $\text{PbC}_6\text{H}_4\text{O}_2$ , from its aqueous solution; while lime water imparts a green color to it if concentrated. Ferric chloride colors its solution dark green, this changes to violet after the addition of a little ammonia, sodium carbonate or tartaric acid. Ferric chloride *imparts a green color to all ortho-dioxy-derivatives* in solution, even if one hydrogen atom is replaced by an alkyl. Pyrocatechin even reduces cold silver solutions, but alkaline copper solutions only upon application of heat.

Acetyl chloride produces the acetyl derivative,  $\text{C}_6\text{H}_4(\text{O.C}_2\text{H}_3\text{O})_2$ , crystallizing in needles. For the nitro-pyrocatechins consult *Ber.*, 15, 2255.

The *monomethyl ether*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O.CH}_3 \\ \diagdown \text{OH} \end{array}$ , **Guaiacol**, occurs in wood-tar and is produced on heating pyrocatechin with potassium hydroxide and potassium methyl sulphate to 180°. It is a colorless liquid, which boils at 200° and has a specific gravity 1.117. It is difficultly soluble in water, readily in alcohol, ether and acetic acid. Ferric chloride gives its alcoholic solution an emerald-green color. It affords salts with the alkali and alkaline earth metals. Its alkaline solutions reduce gold, silver and copper salts. Guaiacol decomposes into pyrocatechin and  $\text{CH}_3\text{I}$  (also  $\text{CH}_3\text{OH}$ ) when heated with hydriodic acid or fused with KOH.

The *dimethyl ether*,  $\text{C}_6\text{H}_4(\text{O.CH}_3)_2$ , is prepared by treating the potassium salt of the mono-methyl ether with  $\text{CH}_3\text{I}$ , and by distilling dimethyl-protocatechuic acid with lime. It is a liquid, which boils at 205°. It is identical with *veratrol*, obtained from veratric acid.

The *carbonic ester*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{CO}$ , results from the action of chlorcarbonic ester upon pyrocatechin, and melts at 118°. Pyrogallol reacts similarly (*Ber.*, 13, 697).

**Resorcin**, Resorcinol,  $\text{C}_6\text{H}_4(\text{OH})_2$  (1, 3), is produced from different resins (like *galbanum* and *asafetida*) and from umbelliferon on fusion with KOH. It results in the same way from (1, 3)-chlor- and iodophenol, from metaphenol sulphonic acid and metabenzene disulphonic acid, also from various other benzene derivatives not included in the meta-series, *e. g.*, from the three brom-benzene sulphonic acids (p. 477) and from both benzene disulphonic acids (compare p. 495).

It was formerly obtained by distilling the extract of Brazil wood; at present,

however, it is prepared technically from crude benzene disulphonic acid (*Journ. pract. Chem.*, 20, 319), and serves for the synthesis of different dyes. It is purified by sublimation and by crystallization from benzene.

Resorcin crystallizes in rhombic prisms or plates, melts at  $118^{\circ}$  when perfectly pure (otherwise at  $102-110^{\circ}$ ) and boils at  $276^{\circ}$ . It dissolves readily in water, alcohol and ether, but not in chloroform and carbon disulphide. Lead acetate does not precipitate the aqueous solution (distinction from pyrocatechin). Silver nitrate is only reduced by it upon boiling; and in the cold if ammonia be present. Ferric chloride colors the aqueous solution a *dark violet*. Bromine water precipitates *tribromresorcin*,  $C_6HBr_3(OH)_2$ , from solution. This crystallizes from hot water in needles. By heating resorcinol with phthalic anhydride we get fluorescein; *the homologous metadioxybenzenes also yield fluoresceins*. With diazo-compounds it forms azo-coloring substances (p. 464).

The *diacetyl compound*,  $C_6H_4(O.C_2H_3O)_2$ , is a liquid. The *diethyl ether*,  $C_6H_4(O.C_2H_5)_2$ , obtained by heating resorcinol with ethyl iodide and potassium hydroxide, boils at  $243^{\circ}$ , the dimethyl ether at  $214^{\circ}$ .

See *Ber.*, 16, 667, for mono- and dinitro-resorcins.

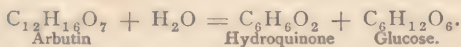
When cold nitric acid acts on resorcinol and various gum-resins (galbanum, gum-ammoniac), or by nitrating metanitrophenol, we get *Trinitro-resorcinol*,  $C_6H(NO_2)_3(OH)_2$  (Styphnic Acid, Oxypicric Acid) (*Ber.*, 17, 259), which crystallizes in yellow hexagonal prisms or plates. It melts at  $175^{\circ}$ , and sublimates when carefully heated, but explodes on rapid heating. It dissolves easily in alcohol and ether, with difficulty in water. Ferrous sulphate and lime water at first color it green, but this disappears (picric acid colors it blood-red). Trinitroresorcinol is a strong dibasic acid, yielding well crystallized, acid and neutral salts. The diethyl ester is solid, and melts at  $120^{\circ}$ .

Amido- and diamido-resorcinol,  $C_6H_3(NH_2)(OH)_2$  and  $C_6H_2(NH_2)_2(OH)_2$ , are obtained by reducing benzene azoresorcin (*Ber.*, 16, 1330) and benzene disazoresorcinol (p. 465) (*Ber.*, 17, 882).

**Hydroquinone**,  $C_6H_4(OH)_2$  (1, 4), was first obtained by the dry distillation of quinic acid and by digesting its aqueous solution with  $PbO_2$ :—



It results also on boiling the glucoside arbutin with dilute sulphuric acid or by the action of emulsin:—



It is synthetically prepared by fusing (1, 4)-iodophenol with KOH at  $180^{\circ}$ ; or from oxysalicylic acid, and from para-amidophenol. Worthy of note is the formation of various hydroquinone derivatives from succino-succinic ester (p. 224), or that of hydroquinone in the distillation of succinates. The most convenient method of preparing it consists in reducing quinone with sulphurous acid:  $C_6H_4O_2 + H_2 = C_6H_6O_2$ .

To get hydroquinone, oxidize aniline in sulphuric acid solution (1 part aniline,



8 parts  $\text{SO}_4\text{H}_2$  and 30 parts  $\text{H}_2\text{O}$ ) with pulverized  $\text{Cr}_2\text{O}_7\text{K}_2$  ( $2\frac{1}{2}$  parts) (*Ber.*, 11, 1104). A more advantageous method consists in first oxidizing aniline to quinone (see this) and reducing the latter to hydroquinone; this is accomplished by conducting  $\text{H}_2\text{S}$  into aqueous quinone until it is decolorized and then extracting the hydroquinone with ether (*Ber.*, 16, 688).

Hydroquinone is dimorphous, crystallizes in monoclinic leaflets and hexagonal prisms, which melt at  $169^\circ$ , and sublime in shining leaflets; it decomposes when quickly heated. It dissolves readily in water, alcohol and ether. It forms crystalline compounds with  $\text{H}_2\text{S}$  and  $\text{SO}_2$ ; these are decomposed by water. Ammonia colors the aqueous solution reddish-brown. It is only in the presence of ammonia that lead acetate produces a precipitate in the solution of hydroquinone. Oxidizing agents (like ferric chloride) convert hydroquinone into quinone; quinhydrone is an intermediate product.

**Methylhydroquinone**,  $\text{C}_6\text{H}_4\begin{smallmatrix} \diagup \text{O}\cdot\text{CH}_3 \\ \diagdown \text{OH} \end{smallmatrix}$ , is formed along with hydroquinone in the decomposition of arbutin with acids or emulsin; and from hydroquinone by heating it with caustic potash, and methyl iodide or potassium methyl sulphate (*Ber.*, 14, 1989). It crystallizes from hot water in hexagonal plates, melts at  $53^\circ$ , and boils at  $243^\circ$ . The *dimethyl ether*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_3)_2$ , melts at  $56^\circ$ , and boils at  $205^\circ$ . The diethyl ether melts at  $66^\circ$ , and boils at  $247^\circ$ .

We obtain the hydroquinone halogen substitution products by direct substitution, or from the substituted quinones and arbutins; and by the addition of  $\text{HCl}$  or  $\text{HBr}$  to quinone:  $\text{C}_6\text{H}_4\text{O}_2 + \text{HCl} = \text{C}_6\text{H}_3\text{Cl}(\text{OH})_2$  (*Ann.*, 209, 105, and 210, 133). *Dinitrohydroquinone*,  $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{OH})_2 + 1\frac{1}{2}\text{H}_2\text{O}$ , from dinitroarbutin, forms golden yellow leaflets, melting at  $135^\circ$ . Alkalies color its aqueous solution a deep violet (*Ann.*, 215, 142).

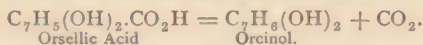
When chloranil (tetrachlorquinone) is digested with a dilute solution of primary sodium sulphite, we get at first tetrachlor-hydroquinone, but later two  $\text{Cl}$ -atoms are replaced by sulphy-groups. The aqueous solution of the resulting dichlor-hydroquinone disulphonic acid,  $\text{C}_6\text{Cl}_2\left\{\begin{smallmatrix} (\text{OH})_2 \\ (\text{SO}_3\text{H})_2 \end{smallmatrix}\right.$ , is colored indigo-blue by ferric chloride. When its alkaline solution is exposed it oxidizes to *potassium euthiochronate*,  $\text{C}_6(\text{OH})_2\left\{\begin{smallmatrix} \text{O}_2 \\ (\text{SO}_3\text{K})_2 \end{smallmatrix}\right.$ . This is a quinone-like compound.

Consult *Ber.*, 16, 688, for hydroquinone sulphonic acids.

**Phenols**,  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH})_2$ , Dioxytoluenes. Four of the six possible isomerides are known. For their reactions see *Ber.*, 15, 2995.

1. **Orcin**, **Orcinol**,  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH})_2$  (1, 3, 5), is found in many lichens of the variety *Roccella* and *Leconora*, partly free and

partly as orsellic acid or erythrine, and is obtained from these acids either by dry distillation or by boiling with lime:—



It is obtained by fusing the extract of aloes with caustic potash. It can be prepared synthetically from dinitro-paratoluidine and various other toluene derivatives by the alteration of their side groups (*Ber.*, 15, 2992). It crystallizes in colorless, six-sided prisms, having 1 molecule  $\text{H}_2\text{O}$ . It dissolves easily in water, alcohol and ether, and has a sweet taste. It melts at  $56^\circ$ , when it contains water, but gradually loses this, and melts (dried in the dessicator) at  $107^\circ$ . It boils at  $290^\circ$ . Lead acetate precipitates its aqueous solution; ferric chloride colors it a *blue violet*. Bleaching lime causes a rapidly disappearing dark violet coloration. It yields azo-coloring substances with diazo-compounds, and therefore has the 2OH-groups in the meta-position (p. 464). It does not form a fluorescein with phthalic anhydride (p. 497).

The orcinol hydroxyl-groups can be replaced by acid and alcohol radicals. The *diethyl ether* boils at  $240\text{--}250^\circ$ . The *monomethyl ether*,  $\text{C}_7\text{H}_6(\text{OH})\cdot\text{O}\cdot\text{CH}_3$ , is identical with so-called *Beta-orcin*, resulting from the distillation of evernic and other lichen acids. Its crystals dissolve readily in water, melt at  $109^\circ$ , and are colored red by ammonia in the air. The *dimethyl ether*,  $\text{C}_7\text{H}_6(\text{O}\cdot\text{CH}_3)_2$ , is a liquid, boils at  $244^\circ$ , and when oxidized with  $\text{MnO}_4\text{K}$  yields the dimethyl ether of symmetrical dioxibenzoic acid.

Orcinol yields the crystalline compound,  $\text{C}_7\text{H}_8\text{O}_2\cdot\text{NH}_3$ , with dry ammonia. On allowing the ammoniacal solution to stand exposed to the air the orcinol changes to orcein,  $\text{C}_7\text{H}_7\text{NO}_3$ , which separates out in the form of a reddish-brown amorphous powder. Orcein forms red lac-dyes with metallic oxides. It is the chief constituent of the coloring matter *archil*, which originates from the same lichens as orcinol through the action of ammonia and air. *Litmus* is produced from the lichens *Rocella* and *Leconora*, by the action of ammonia and potassium carbonate. The concentrated blue solution of the potassium salt, when mixed with chalk or gypsum, constitutes the commercial litmus.

2. **Iso-orcin**,  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH})_2$  (1, 2, 4— $\text{CH}_3$  in 1) (Cresorcin,  $\gamma$ -orcin), is obtained by fusing  $\alpha$ -toluene disulphonic acid with KOH; also from nitro-paratoluidine and  $\alpha$ -toluylene diamine (*Ber.*, 15, 2835 and 2981). It forms soluble needles, melting at  $104^\circ$ , and boiling at  $270^\circ$ . It gives a *violet* coloration with ferric chloride, and affords a fluorescein with phthalic anhydride.

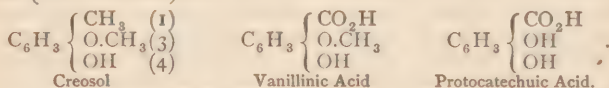
3. **Homopyrocatechin**,  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH})_2$  (1, 3, 4— $\text{CH}_3$  in 1), is formed from its methyl ether, creosol, when heated with hydriodic acid, and by the distillation of homoprotocatechuic acid. It has been synthetically prepared from meta-nitro-para-toluidine (*Ber.*, 15, 2983). It is a non-crystallizable syrup; otherwise it is

like pyrocatechin. It reduces Fehling's solution and a silver solution, even in the cold, and is colored *green* by ferric chloride.

Its *monomethyl ether* is the so-called **Creosol**,  $C_6H_3(CH_3)(O.CH_3)$  (3), (4), formed from guaiacum resin and found in beech-wood-tar.

That fraction of the beech-wood-tar (creasote p. 480), boiling at  $220^\circ$ , consists chiefly of creosol and phlorol. Potassium-creosol is precipitated on adding alcoholic potash to the ethereal solution; potassium phlorol remains dissolved (*Ber.*, 10, 57; 14, 2010).

Creosol boils at  $220^\circ$ , and is very similar to guaiacol (p. 496). It reduces silver nitrate on warming, and in alcoholic solution is colored a dark green by ferric chloride. It yields an *acetate* with acetic acid, which by oxidation with  $MnO_4K$  and saponification with  $KOH$  affords *vanillinic acid*. Its *methyl ether*,  $C_6H_3(CH_3)(O.CH_3)_2$  (methyl creosol, dimethyl-homo-pyrocatechin), boils at  $214-218^\circ$ , and when oxidized with  $MnO_4K$  yields dimethyl-protocatechuic acid. The relations of these substances are seen in the following formulas (see Vanillin):—



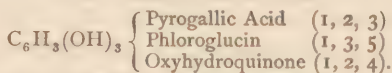
4. **Toluhydroquinone**,  $C_6H_3(CH_3)(OH)_2$  (1, 4,  $CH_3$ ), is produced by the reduction of tolu-quinone (p. 504) with sulphurous acid, and from nitro-ortho-toluidine (*Ber.*, 15, 2981). It consists of needles dissolving easily in water, alcohol and ether, and melting at  $124^\circ$ . It resembles hydroquinone very much, and with toluquinone yields a quinhydrone. Caustic soda colors it bluish-green, then dark brown.

**Xylohydroquinone**,  $C_6H_2(CH_3)_2(OH)_2$ , Dioxyparaxylene, results on the reduction of xylo-quinone (p. 504), and is identical with so-called *hydrophlorol*, obtained from phlorol (*ibid*). It crystallizes from hot water in pearly leaflets, melting at  $212^\circ$ .

**Mesorcin**,  $C_6H(CH_3)_3(OH)_2 = C_9H_{12}O_2$ , dioxymesitylene, from dinitromesitylene, sublimes in shining leaflets, melts at  $150^\circ$ , and distils at  $275^\circ$ . When boiled with a ferric chloride solution, a methyl group splits off and oxyxylo-quinone results (p. 505).

**Thymo-hydroquinone**,  $C_{10}H_{12}(OH)_2 = C_6H_2(CH_3)(C_3H_7)(OH)_2$ , has been obtained by the reduction of thymoquinone, and forms four-sided, shining prisms, melting at  $139^\circ$ .

### TRIVALENT PHENOLS.



1. **Pyrogalllic Acid**,  $C_6H_3O_3$ , **Pyrogallol**, is formed by heating gallic acid alone, or better, with water, to  $210^\circ$ :—



and by fusing the two parachlorophenol-disulphonic acids and hæmatoxylin with potassium hydroxide. It forms white leaflets or needles, melts at  $115^{\circ}$ , and sublimes when carefully heated. It dissolves readily in water, more difficultly in alcohol and ether. Its alkaline solution absorbs oxygen very energetically, turns brown and decomposes into  $\text{CO}_2$ , acetic acid and brown substances. Pyrogallol quickly reduces salts of mercury, silver and gold with precipitation of the metals, while it is oxidized to acetic and oxalic acids. Ferrous sulphate containing ferric oxide colors its solution blue, ferric chloride red. Lead acetate precipitates white  $\text{C}_6\text{H}_6\text{O}_3 \cdot \text{PbO}$ . An iodine solution imparts a purple-red color to an aqueous or alcoholic pyrogallol solution. Gallic and tannic acids react similarly.

Acetyl chloride converts pyrogallol into its *triacetyl ester*,  $\text{C}_6\text{H}_3(\text{O.C}_2\text{H}_3\text{O})_3$ , which is not very soluble in water. The *dimethyl ether*,  $\text{C}_6\text{H}_3(\text{O.CH}_3)_2.\text{OH}$ , is found in that fraction of beech-wood tar boiling at  $250\text{--}270^{\circ}$ . Separated in a pure form from its benzoyl compound, it crystallizes in white prisms, melting at  $51\text{--}52^{\circ}$ , and boiling at  $253^{\circ}$ . When heated with hydrochloric acid it breaks up into pyrogallol and methyl chloride. Different oxidizing agents (potassium bichromate and acetic acid) convert it into *carulignone*, a diphenyl derivative. When the acetyl-derivative of the dimethyl ether is oxidized, the acetyl group separates and the quinone compound,  $\text{C}_6\text{H}_2(\text{O.CH}_3)_2\text{O}_2$ , results. The triethyl ether is formed on heating pyrogallol with caustic potash and potassium ethyl sulphate, also from triethyl-pyrogallo-carboxylic acid (see this). It melts at  $39^{\circ}$ .

2. **Phloroglucin**,  $\text{C}_6\text{H}_6\text{O}_3 = \text{C}_6\text{H}_3(\text{OH})_3$  (1, 3, 5), is obtained from different resins (catechu, kino), on fusion with caustic potash; also by the decomposition of phloretin and quercetin (see these), and by the fusion of resorcinol and resorcinol disulphonic acid with sodium hydroxide. It crystallizes in large, colorless prisms with  $2\text{H}_2\text{O}$ ; these effloresce in the air. It loses all its water of crystallization at  $110^{\circ}$ , melts at  $220^{\circ}$ , and sublimes without decomposition. It has a sweetish taste, and dissolves readily in water, alcohol and ether. Lead acetate does not precipitate it; ferric chloride colors its solution a *dark violet*. Phloroglucin affords *phloramine*,  $\text{C}_6\text{H}_3 \left\{ \begin{smallmatrix} (\text{OH})_2 \\ \text{NH}_2 \end{smallmatrix} \right.$ , with ammonia. This yields crystalline salts with the acids. Chlorine oxidizes phloroglucin to dichloroacetic acid.

The *dibutyryl ester*,  $\text{C}_6\text{H}_3 \left\{ \begin{smallmatrix} \text{OH} \\ (\text{O.C}_4\text{H}_7\text{O})_2 \end{smallmatrix} \right.$ , occurs in the root of *Aspidium filix*. It is a crystalline substance, which affords phloroglucin and butyric acid when fused with KOH.

3. **Oxyhydroquinone**,  $\text{C}_6\text{H}_3(\text{OH})_3$  (1, 2, 4), is produced on fusing hydroquinone with KOH. It is crystalline, very soluble in alcohol and ether, and in aqueous solution soon acquires a dark color. Ferric chloride colors it a dark greenish-brown (*Ber.*, 16, 1231).

**Methyl pyrogallol**,  $\text{C}_6\text{H}_2(\text{CH}_3)(\text{OH})_3$ , and **Propyl pyrogallol**,  $\text{C}_6\text{H}_2(\text{C}_3\text{H}_7)(\text{OH})_3$ , occur in beech-wood tar as dimethyl ether (p. 480); the latter is identical with so-called *picamar*.

A *tetravalent* phenol, **Tetraoxybenzene**,  $\text{C}_6\text{H}_2(\text{OH})_4$ , has been obtained as a dimethyl ether,  $\text{C}_6\text{H}_2(\text{O.CH}_3)_2.(\text{OH})_2$ , from the corresponding quinone, which is formed by the oxidation of dimethyl-propyl-pyrogallol (*Ber.*, 16, 332).

The compound produced by the addition of aqueous hypochlorous acid to benzene,  $\text{C}_6\text{H}_6 \left\{ \begin{smallmatrix} \text{Cl} \\ (\text{OH})_3 \end{smallmatrix} \right.$ , may be considered an addition product of a trivalent phe-

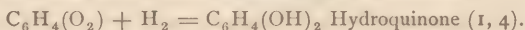


nol. It consists of colorless leaflets, melting at  $10^{\circ}$ , and dissolving with difficulty in water, but readily in alcohol and ether. When digested with a dilute sodium carbonate solution it is altered to *Phenose*,  $C_6H_{12}O_6 = C_6H_6(OH)_6$ . This resembles the glucoses. It is an amorphous, deliquescent substance, readily soluble in water and alcohol. It reduces an ammoniacal copper solution, but does not ferment. When heated with hydriodic acid phenose is converted into hexyl iodide,  $C_6H_{13}I$ .

### QUINONES.

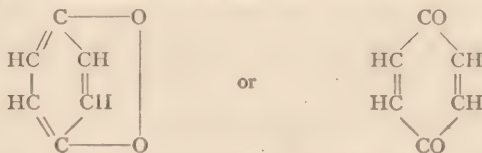
This is the designation ascribed to all derivatives of benzene in which 2H-atoms are replaced by 2O-atoms. They are mostly produced by the direct oxidation of benzenes, especially the condensed varieties (naphthalene, anthracene, chrysene, phenanthrene) with chromic acid in glacial acetic acid. These compounds, however, do not possess uniform character, hence various quinone groups are noted.

The *true quinones* or *para-quinones*, whose prototype is ordinary quinone or benzoquinone,  $C_6H_4O_2$ , are yellow colored, volatile compounds, having a peculiar, penetrating quinone odor, and are rarely volatilized with steam. Reducing agents ( $SO_2$ , conc-HI) easily convert them, with absorption of 2H-atoms, into the corresponding colorless dioxy-compounds (hydroquinones):—



Hence they oxidize readily, and may be compared to the peroxides (like acetyl peroxide  $(C_2H_3O)_2O_2$ ). The two oxygen atoms take the para-position in the benzene nucleus, and the para-quinones therefore are readily produced by oxidation of the para-derivatives of the benzenes.

It is usually supposed that in the ordinary quinones the 2O-atoms are linked by one valence to each other; it is, however, possible, that they ought to be considered as di-ketones having 2CO-groups:—



The fact that in the different reactions the 2O-atoms are invariably separated by only two monovalent atoms or groups (in the action of  $PCl_5$ ) forming normal benzene derivatives,  $C_6X_6$ ; furthermore, the simple relations of the quinones to the quinone-chlorimides and indophenols (p. 505), and to the quinones with two nuclei (see below), argue for the first view. That the quinones, like the ketones, combine with hydroxylamine-hydrochloride, forming compounds (the so-called nitrosophenols, p. 485), in which 1O-atom is replaced by the oximido-group,  $N.OH$  (*Ber.*, 17, 214), appears to support the idea of their ketone nature. The quinones react similarly with phenyl hydrazine (*Ber.*, 16, 1563), (see also *Ann.*, 223, 196).

Another series of so-called quinones ( $\beta$ -naphthaquinone, anthraquinone, phenanthraquinone) must be considered true diketones (with 2CO-groups). They are not volatile and odorless, and are either *para-diketones* (like anthraquinone) or *ortho-diketones* (e. g.,  $\beta$ -naphthaquinone and phenanthraquinone). Sulphurous acid reduces the latter to the corresponding hydroquinones; they form anhydro-compounds with the aldehydes and ammonia (*Ber.*, 15, 1451).

There exist, finally, the quinones with two nuclei, e. g., cœrulignone, derived from diphenyl. In these the 2O-atoms link two benzene nuclei.

**Quinone**,  $C_6H_4O_2$ , Benzoquinone, was first obtained by distilling quinic acid with  $MnO_2$  and sulphuric acid. It is formed from many benzene compounds, especially those di-derivatives belonging to the para-series (e. g., para-phenylene-diamine, amidophenol, phenol sulphonic acid and sulphanilic acid), when they are oxidized with  $MnO_2$  and sulphuric acid, or with a diluted chromic acid mixture. Benzidine,  $C_{12}H_8(NH_2)_2$ , likewise affords considerable quantities of quinone. Hydroquinone is oxidized to quinone even on boiling with a ferric chloride solution. It is, however, best prepared (according to Nietzki) by oxidizing aniline with chromic acid.

*Preparation.*—Dissolve 1 part aniline in 8 parts sulphuric acid diluted with 10 parts water, gradually add  $3\frac{1}{2}$  parts  $K_2Cr_2O_7$ , dissolved in 2 parts  $H_2O$ , to the cooled solution; let the whole stand twelve hours and then extract the quinone with ether (*Ber.*, 16, 687).

Quinone crystallizes in golden-yellow prisms, melts at  $116^\circ$ , and sublimes at medium temperatures, in shining needles. Its vapor density confirms the formula  $C_6H_4O_2$ . It possesses a peculiar, penetrating odor, distils readily with steam, and dissolves easily in hot water, alcohol and ether. It turns brown on exposure to sunlight. Reducing agents ( $SO_2$ , Zn and HCl) convert it first into quinhydrone and then into hydroquinone.  $PCl_5$  changes it to para-dichlorbenzene,  $C_6H_4Cl_2$ .

Quinone affords chlor- and brom-hydroquinone with concentrated hydrochloric and hydrobromic acids (p. 498). It also unites with two molecules of acetyl chloride to form diacetyl-chlorhydroquinone,  $C_6H_4O_2 + 2C_2H_3OCl = C_6H_3Cl(O.C_2H_3O)_2 + HCl$  (*Ber.*, 16, 2096). Quinone yields para-nitrosophenol (p. 486) with hydroxylamine hydrochloride. With ammonia and the primary amines it yields compounds in which one and two aniline residues enter the benzene nucleus (*Ber.*, 16, 1555). Hydroquinone is produced at the same time.

Chlor- and brom-quinones are obtained by the substitution of quinone or by the oxidation of substituted hydroquinones (p. 498) with nitric acid.

*Trichlorquinone*,  $C_6HCl_2(O_2)$ , is produced together with *tetrachlorquinone*; it consists of large, yellow plates, melting at  $166^\circ$ . It forms tetrachlorhydroquinone,  $C_6Cl_4(OH)_2$ , by heating with fuming hydrochloric acid. Fuming nitric acid oxidizes this product to tetrachlorquinone.

*Tetrachlorquinone*,  $C_6Cl_4(O_2)$ , **Chloranil**, is obtained together with trichlorquinone from many benzene compounds (aniline, phenol, isatin) by the action of chlorine or potassium chlorate and hydrochloric acid. Its production from symmetrical tetrachlorbenzene (p. 423) by boiling with nitric acid is theoretically interesting.

In order to prepare it, gradually add a mixture of phenol (1 part) with  $\text{ClO}_3\text{K}$  (4 parts) to concentrated hydrochloric acid, diluted with an equal volume of water, and apply a gentle heat. At first red crystals separate out, but on the addition of more  $\text{ClO}_3\text{K}$  these become yellow. The crystalline mass consists of tri- and tetra-chloroquinone. To effect their separation, they are changed by  $\text{SO}_2$  to hydroquinones (tetrachlorhydroquinone is insoluble in water) and the latter oxidized with nitric acid (*Ber.*, 10, 1792, and *Ann.*, 210, 174).

Chloranil consists of bright golden leaflets, insoluble in water, but soluble in hot alcohol and ether. It sublimes about  $150^\circ$ , in yellow leaflets.  $\text{PCl}_5$  converts it into  $\text{C}_6\text{Cl}_6$ . It oxidizes and serves as an oxidizing agent in the manufacture of coloring matters. Chloranil dissolves with a purple-red color in  $\text{KOH}$ , forming potassium chloranilate,  $\text{C}_6\text{Cl}_2(\text{O}_2)(\text{OK})_2 + \text{H}_2\text{O}$ , which crystallizes in dark red needles, not very soluble in water. Acids set free chloranilic acid,  $\text{C}_6\text{Cl}_2(\text{O}_2)(\text{OH})_2 + \text{H}_2\text{O}$ , which consists of red, shining scales. Aqueous ammonia converts chloranil into chloranilamide,  $\text{C}_6\text{Cl}_2(\text{O}_2)(\text{NH}_2)_2$ , and chloranilamic acid,  $\text{C}_6\text{Cl}_2(\text{O}_2)(\text{NH}_2)\text{OH}$ .

The brom-quinones are perfectly analogous to the chlorine derivatives. Tetra-bromquinone, **Bromanil**,  $\text{C}_6\text{Br}_4\text{O}_2$ , is obtained by heating phenol (1 part) with 10 parts bromine and 3 parts iodine in 50 parts water. It consists of golden-yellow, shining leaflets or thick plates, which melt and sublime.

**Nitranilic Acid**,  $\text{C}_6(\text{NO}_2)_2\text{O}_2(\text{OH})_2$ , analogous to chloranilic acid, is formed from hydroquinone with nitrous acid; more readily from diacetyl-hydroquinone with fuming nitric acid (*Ber.*, 16, 2093). Large, hygroscopic crystals. It is a strong acid.

The phenols combine directly with the phenols yielding crystalline compounds, in which are combined 2 molecules of the monovalent phenols (*Ann.*, 215, 134). **Phenoquinone**,  $\text{C}_6\text{H}_4\text{O}_2 \cdot 2\text{C}_6\text{H}_5(\text{OH})$ , consists of red needles, which dissolve readily in alcohol and ether, melt at  $71^\circ$ , and readily volatilize.

An analogous compound is—

**Quinhydrone**,  $\text{C}_{12}\text{H}_{10}\text{O}_4 = \text{C}_6\text{H}_4\text{O}_2 \cdot \text{C}_6\text{H}_4(\text{OH})_2$ . This is produced by the direct union of quinone with hydroquinone. It appears as an intermediate product in the reduction of quinone or in the oxidation of hydroquinone. It consists of green prisms or leaflets with metallic lustre, melts readily, and dissolves in hot water with a brown, in alcohol and ether with a green, color. When it is boiled with water it decomposes into hydroquinone and quinone, which distils over. It is changed by oxidation to quinone, and by reduction to hydroquinone.

The homologous quinones are quite similar to benzoquinone.

**Toluquinone**,  $\text{C}_6\text{H}_3(\text{CH}_3)\text{O}_2$ , is obtained from  $\epsilon$ -diamido-toluene (p. 454), which is formed by the splitting-up of ortho- and meta-amido-azo-toluene (p. 464), and contains the 2 amido-groups in the para-position. It is most conveniently prepared by oxidizing ortho-toluidine (crude) with chromic acid, just as in the case of benzoquinone. It consists of golden yellow leaflets, melting at  $67^\circ$ ; these are very volatile and have the quinone odor. Reduction (with  $\text{SO}_2$ ) converts it into tolu-hydroquinone (p. 500). Chlorinated toluquinones are obtained by the action of potassium chlorate and hydrochloric acid upon cresols,  $\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$ .

**Xyloquinone**,  $\text{C}_6\text{H}_2(\text{CH}_3)_2\text{O}_2$  (1, 4,  $\text{O}_2$ ), results by the oxidation of para-xylydine (p. 453), or more readily from diamido-xylene (obtained by the decom-

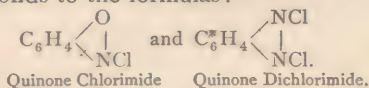
position of amido-azo-xylidine) by means of  $\text{Cr}_2\text{O}_7\text{K}_2$ , and sulphuric acid. It is identical with *phloron* (*Ann.*, **215**, 170). It consists of golden yellow needles, which resemble quinone in odor, and melt at  $125^\circ$ .  $\text{SO}_2$  reduces it to xylohydroquinone (p. 500).

Oxy-*m*-xyloquinone,  $\text{C}_6\text{H}(\text{CH}_3)_2(\text{OH})\text{O}_2 = \text{C}_8\text{H}_8\text{O}_3$ , is formed on oxidizing diamido- or dioxy-mesitylene (Mesorcin, p. 500) with ferric chloride, by which, rather singularly, a methyl group is displaced (*Ber.*, **15**, 1377). It sublimes in golden yellow needles, with a quinone odor, and melts at  $123^\circ$ . Alkaline bodies color its aqueous solution a red violet.

Thymo-quinone,  $\text{C}_6\text{H}_2(\text{CH}_3)(\text{C}_3\text{H}_7)\text{O}_2$ , Thymoöl, is formed by oxidizing thymol or carvacrol (p. 500) with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ , or amidothymol with ferric chloride. It forms yellow plates, melts at  $45.5^\circ$ , and distils at  $200^\circ$ . Oxythymo-quinone,  $\text{C}_{10}\text{H}_{11}(\text{OH})\text{O}_2$ , melts at  $167^\circ$  (*Ber.*, **16**, 901), and affords a dioxy-thymoquinone,  $\text{C}_{10}\text{H}_{10}(\text{OH})_2\text{O}_2$ , from which thymodiquinone,  $\text{C}_{10}\text{H}_{10}(\text{O}_2)$  ( $\text{O}_2$ ), is obtained by oxidation.

### QUINONE-CHLORIMIDES.

These are very similar to the quinones, and possess an analogous constitution (p. 502). We must regard them either as diketones or peroxides, in which oxygen is replaced by the group  $\text{NCl}$ . The latter view corresponds to the formulas:—



They are produced from para-amidophenols and para-phenylene diamines (their  $\text{HCl}$ -salts) by oxidation with an aqueous solution of bleaching lime. The mono-chlorimides form the indophenol coloring matters (see below) with phenols and tertiary anilines.

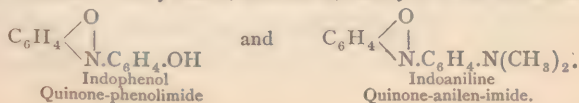
Quinone Chlorimide,  $\text{C}_6\text{H}_4(\text{ONCl})$ , produced from  $\text{HCl}$ -para-amidophenol with bleaching lime (*Jour. pr. Chem.* **23**, 435), forms golden yellow crystals, which melt at  $85^\circ$ , volatilize readily with steam and smell like quinone. It is easily soluble in hot water, alcohol and ether. Reducing agents (also  $\text{H}_2\text{S}$ ) convert it into para-amidophenol. When boiled with water it decomposes into  $\text{NH}_4\text{Cl}$  and quinone.

Quinone-dichlorimide,  $\text{C}_6\text{H}_4(\text{N}_2\text{Cl}_2)$ , from paraphenylene diamine-hydrochloride, crystallizes in needles, which deflagrate at  $124^\circ$ , and are converted by reducing agents into para-phenylene-diamine.

Dibrom-quinone-chlorimide,  $\text{C}_6\text{Br}_2\text{H}_2(\text{ONCl})$ , from dibrom-para-nitrophenol, crystallizes in dark yellow prisms, melting at  $80^\circ$  and decomposing at  $121^\circ$ . Trichlor-quinone-chlorimide,  $\text{C}_6\text{Cl}_3\text{H}(\text{ONCl})$ , from trichlor-para-amidophenol, forms yellow prisms, melting at  $118^\circ$ .

### INDOPHENOLS AND INDOANILINES.

We may consider the following compounds as prototypes of these dye-substances. They have, however, not yet been isolated:—



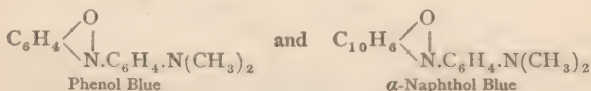


The indophenols are produced by the action of the quinone-chlorimides upon the warm phenols, or upon their aqueous solutions at ordinary temperatures, and by the oxidation of a mixture of a para-amido-phenol with a phenol (1 molecule each). They dissolve in alcohol with a red color and possess a phenol-like character. Their alkali and ammonia salts dissolve with a blue color in water.

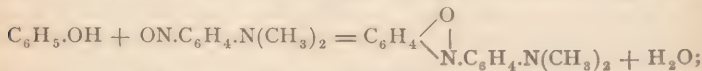
**Dibrom-quinone-phenolimide**,  $C_6H_2Br_2 \begin{smallmatrix} \diagup O \\ | \\ N.C_6H_4.OH \end{smallmatrix}$ . Its sodium salt is

produced when alcoholic dibrom-quinone-chlorimide acts on an alkaline phenol solution. It separates in golden-green crystals, which dissolve readily in water, imparting to it a blue color. When the alkaline solution is digested the blue color becomes pale red, but reappears on cooling in contact with air. Acetic acid precipitates *free* dibromphenolimide from the sodium salt; it crystallizes in dark red, shining prisms, and is soluble in alcohol and ether with a fuchsine-red color. Mineral acids decompose it into dibromamidophenol and quinone. By reduction with grape sugar in alkaline solution it is transformed into leuco-dibromquinone phenolimide,  $C_6H_2Br_2 \begin{smallmatrix} \diagup OH \\ | \\ NH.C_6H_4.OH \end{smallmatrix}$ ; this is a dibromdioxy-diphenylamine, (p. 440). Hence the *indophenols* can also be considered as *derivatives* of *di-oxydiphenylamine*. They contain the *chromophor-group*,  $O-N$ , with nitrogen linked to two benzene nuclei (*Ber.*, 16, 2849).

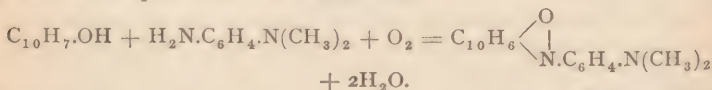
The indoanilines, *e. g.* :—



are produced : (1) by the action of quinone-chlorimides upon an alcoholic solution of dimethyl aniline ; (2) by the action of nitroso-dimethyl aniline upon phenol and  $\alpha$ -naphthol in alkaline solution, especially in the presence of reducing agents :—



(3) by oxidation of a mixture of dimethyl-para-phenylene-diamine (p. 454) with phenol and  $\alpha$ -naphthol in alkaline solution :—



The indoanilines are distinguished from the indophenols by their inability to form salts with the alkalis. They are feeble bases, but are rather stable in the presence of alkalis. Acids decompose them into quinones and dimethyl-para-phenylene diamines. They have an intense blue color and are substituted for indigo in color dye-printing. Reducing agents decolorize them, as they absorb two hydrogen atoms and pass into dimethyl-amido-oxy-diphenylamines, *e. g.*,  $NH \begin{smallmatrix} \diagup C_6H_4.OH \\ | \\ C_6H_4.N(CH_3)_2 \end{smallmatrix}$  (p. 440). Hence they are intimately related to the blue dyes of the phenylene-blue series and to the safranines (p. 469) (*Ber.*, 16, 2855).

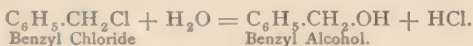
## ALCOHOLS.

The *true alcohols* (isomeric with the phenols) of the benzene series are produced by the entrance of hydroxyls into the side-chains of the homologous benzenes (p. 404). They are perfectly analogous to the fatty alcohols. By oxidation they yield aldehydes or (ketones) and acids:—

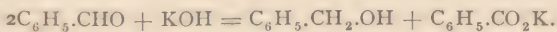


The methods of forming them are perfectly analogous to those of the fatty-series. They are obtained:—

1. By the conversion of substituted hydrocarbons, like benzyl chloride,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{Cl}$ , into acid esters, and saponifying the latter with alkalis, or by boiling the chlorides with water and lead oxide (p. 89), or with a soda solution:—

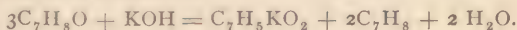


2. By the action of nascent hydrogen (p. 90) on the aldehydes and ketones, or by heating the aldehydes, or letting them stand with alcoholic or aqueous potash, whereby acids are formed at the same time:—



In this series we also distinguish primary, secondary and tertiary alcohols.

**Benzyl Alcohol**,  $\text{C}_7\text{H}_8\text{O} = \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH}$ , occurs as benzylbenzoic ester, and benzyl-cinnamic ester in the balsams of Peru and Tolu, and in storax, and can be obtained from benzaldehyde (oil of bitter almonds) by the action of sodium amalgam or aqueous potassium hydroxide (*Ber.*, 14, 2394), or by boiling benzyl chloride with a soda solution. It is a colorless liquid, with a faint aromatic odor, and boils at  $206^\circ$ ; its specific gravity at  $0^\circ$  is 1.062. It is difficultly soluble in water, but readily in alcohol and ether. It yields benzaldehyde and benzoic acid when oxidized. Heated with hydrochloric acid or hydrobromic acid, the OH-group is replaced by halogens. Benzoic acid and toluene result on distilling with concentrated potash:—



The *esters* of benzyl alcohol are produced from it by the action of acid chlorides, or from benzyl chloride by boiling with organic salts. The *acetic ester*,  $\text{C}_7\text{H}_7\text{O}\cdot\text{C}_2\text{H}_3\text{O}$ , is liquid and boils at  $206^\circ$ . The *oxalic ester*,  $\text{C}_2\text{O}_4(\text{C}_7\text{H}_7)_2$ , forms shining leaflets, melting at  $80^\circ$ .

The *alcohol ethers* are obtained by heating benzyl chloride with sodium alcohols. The *methyl ether*,  $\text{C}_7\text{H}_7\text{O}\cdot\text{CH}_3$ , boils at  $168^\circ$ ; the *ethyl ether* at  $185^\circ$ .

The *dibenzyl ether*,  $(\text{C}_6\text{H}_5\cdot\text{CH}_2)_2\text{O}$ , is formed on heating the alcohol with boric anhydride, and benzyl chloride with water to  $190^\circ$ . It is an oil boiling near  $310^\circ$ .

The *benzyl-phenyl ether*,  $C_6H_5.CH_2.O.C_6H_5$ , results when benzyl chloride is heated together with potassium phenolate,  $C_6H_5.OK$ . It melts at  $39^\circ$ , and boils at  $287^\circ$ .

Substituted benzyl alcohols are derived from substituted benzyl chlorides, *e. g.*  $C_6H_4Cl.CH_2Cl$ , when they are heated with aqueous ammonia, or by means of acetic esters. *Para-chlor-benzyl alcohol*,  $C_6H_4Cl.CH_2.OH$ , consists of long needles, which melt at  $66^\circ$ , and boil without decomposition.

*o-Nitrobenzyl Alcohol*,  $C_6H_4(NO_2).CH_2.OH$ , is formed by shaking *ortho*-nitrobenzaldehyde (crude) with concentrated sodium hydroxide, and crystallizes in bright yellow needles, melting at  $74^\circ$ . *m-Nitrobenzyl Alcohol*, from *meta*-nitrobenzaldehyde, is a thick, yellow oil; its chloride melts at  $46^\circ$ .

*p-Nitrobenzyl Alcohol* is obtained from its chloride and from nitrobenzyl acetic ester. It melts at  $93^\circ$ .

*o-Amidobenzyl Alcohol*,  $C_6H_4(NH_2).CH_2.OH$ , is formed by the reduction of anthranil and *ortho*-nitrobenzyl alcohol with zinc dust and hydrochloric acid. It crystallizes in white needles, has an aniline odor, and melts at  $82^\circ$  (*Ber.*, 15, 2109).

**Benzyl Sulphydrate**,  $C_6H_5.CH_2.SH$ , Benzyl Mercaptan. This is formed by the action of alcoholic KSH upon benzyl chloride. It is a liquid, with a leek-like odor; boils at  $194^\circ$ , and at  $20^\circ$  has a specific gravity = 1.058. Salts of the heavy metals precipitate mercaptides from its alcoholic solutions. On exposure it oxidizes to **Benzyl disulphide**,  $(C_6H_5)_2S_2$ , which crystallizes from alcohol in shining leaflets melting at  $66^\circ$ . Nascent hydrogen causes it to revert to benzyl sulphydrate.

**Benzyl Sulphide**,  $(C_6H_5.CH_2)_2S$ , is formed by the action of  $K_2S$  upon an alcoholic solution of benzyl chloride. Colorless needles, melting at  $49^\circ$ . Nitric acid oxidizes it to the oxy-sulphide,  $(C_6H_5.CH_2)_2SO$ , which dissolves in hot water and melts at  $130^\circ$ . The *sulphone*,  $(C_6H_5.CH_2)_2SO_2$ , melts at  $150^\circ$ .

*Potassium Benzylsulphonate*,  $C_6H_5.CH_2.SO_3K + H_2O$ , is formed on boiling benzyl chloride with potassium sulphite. The free acid is a deliquescent crystalline mass; it is isomeric with toluene-sulphonic acid.

Alcoholic ammonia converts benzyl chloride into mono-, di-, and tri-benzylamines, which are separated by means of their hydrochloric acid salts. **Benzylamine**,  $C_6H_5.CH_2.NH_2$  (Benzamine), is formed when zinc and hydrochloric acid act upon benzonitrile; it dissolves in water and boils at  $183^\circ$ . It affords a crystalline salt with  $CO_2$ . **Dibenzylamine**,  $(C_6H_5)_2NH$ , is a liquid, and is insoluble in water. **Tribenzylamine**,  $(C_6H_5)_3N$ , forms large plates, melting at  $91^\circ$ , and distilling near  $300^\circ$  undecomposed. Its hydrochloride is insoluble in water.

Substituted benzylamines are derived from substituted benzyl chlorides.

**Alcohols**,  $C_8H_{10}O$ . There are five isomerides.

**Tolyl Alcohols**,  $C_6H_4(CH_3).CH_2.OH$ . The *ortho*-body (1, 2), obtained from *orthotoluy*l aldehyde with sodium amalgam, melts at  $54^\circ$ , and boils at  $210^\circ$ . The *para*, derived from *paratoluy*l aldehyde with potassium, melts at  $59^\circ$ , and boils at  $217^\circ$ .

**Phenyl Ethyl Alcohol**,  $C_6H_5.CH_2.CH_2.OH$ , *α*-Tolyl alcohol, obtained from *α*-toluyaldehyde, is a liquid boiling at  $212^\circ$ , has a specific gravity = 1.033 at  $20^\circ$ , and when moderately oxidized yields *α*-toluic acid. Its acetic ester boils at  $224^\circ$ .

**Phenyl Methyl Carbinol**,  $C_6H_5 \cdot CH(OH) \cdot CH_3$ , is a secondary alcohol, produced from  $\beta$ -brom-ethyl benzene (p. 416), and by the action of sodium amalgam upon acetophenone,  $C_6H_5 \cdot CO \cdot CH_3$ . It boils at  $203^\circ$ . Oxidation converts it back into acetophenone. The acetic ester boils near  $214^\circ$ , and partly decomposes into acetic acid and styrol.

**Phenyl-Propyl Alcohol**,  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2(OH)$ , Hydrocinnamic Alcohol, obtained from cinnamic alcohol, boils at  $235^\circ$ . Its specific gravity at  $18^\circ$  is 1.008. It exists as cinnamic ester in storax. Secondary **Phenyl-ethyl Carbinol**,  $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CH_3$ , is formed from phenyl-ethyl ketone,  $C_6H_5 \cdot CO \cdot C_2H_5$ , and boils at  $210^\circ$ .

**Cumin Alcohol**,  $C_6H_4 \cdot \begin{smallmatrix} \diagup C_3H_7 \\ CH_2 \cdot OH \end{smallmatrix}$  (1, 4), contains the isopropyl-group. It is formed from cuminic aldehyde. It boils at  $243^\circ$ , and yields common cymene,  $C_{10}H_{14}$ , when boiled with zinc dust. Its chloride,  $C_6H_4(C_3H_7) \cdot CH_2Cl$ , affords the same product, when heated with zinc and hydrochloric acid. Boiling alcoholic potash or dilute nitric acid oxidizes it to cuminic acid. Its isomeride is tertiary—

**Benzyl-dimethyl Carbinol**,  $C_6H_5 \cdot \begin{smallmatrix} CH_2 \\ (CH_3)_2 \end{smallmatrix} \cdot C \cdot OH$ , produced by acting on  $\alpha$ -toluic chloride,  $C_6H_5 \cdot CH_2 \cdot COCl$ , with zinc methyl. Long needles, which melt at  $20-22^\circ$ , and boil about  $225^\circ$ .

**Sycoceryl Alcohol** forms needles, melting at  $90^\circ$ . It exists as acetate,  $C_{18}H_{29} \cdot O \cdot C_2H_3O$ , in the resin of *Ficus rubiginosa*. This compound melts at  $119^\circ$ .

## DIVALENT (DIHYDRIC) ALCOHOLS.

Dihydric **Benzylene-Glycol**,  $C_6H_5 \cdot CH(OH)_2$ , would correspond to methylene glycol, but does not exist. Where it should occur benzaldehyde appears (p. 253). Its ethers are derived from benzylene chloride,  $C_6H_5 \cdot CHCl_2$ , through the action of sodium alcoholates or salts of organic acids. The *dimethyl ether*,  $C_6H_5 \cdot CH(O \cdot CH_3)_2$ , boils at  $205^\circ$ ; the *diethyl ether* at  $217^\circ$ . The *acetate*,  $C_6H_5 \cdot CH(O \cdot C_2H_3O)_2$ , is crystalline, melts at  $43^\circ$ , and boils with decomposition at  $220^\circ$ .

**Tollylene Alcohol**,  $C_8H_{10}O_2 = C_6H_4 \cdot \begin{smallmatrix} \diagup CH_2 \cdot OH \\ CH_2 \cdot OH \end{smallmatrix}$  (1, 4), is obtained from tollylene bromide,  $C_6H_4(CH_2Br)_2$  (by introduction of bromine into boiling para-xylene); it forms crystals, dissolves easily in water, and melts at  $113^\circ$ . The *acetate* consists of leaflets, melting at  $47^\circ$ . It yields terephthalic acid when oxidized. **Phthalyl Alcohol**,  $C_6H_4(CH_2 \cdot OH)_2$  (1, 2), is isomeric with the preceding. It is formed from the chloride of phthalic acid,  $C_6H_4(CO \cdot Cl)_2$ , by the action of sodium amalgam, and from ortho-xylene bromide (p. 415) on boiling it with a soda solution. It is a granular, crystalline mass, melting slowly from  $56-72^\circ$ . Potassium permanganate oxidizes it to phthalic acid. It yields ortho-xylene when heated with HI and phosphorus to  $180^\circ$ .

**Styrolene Alcohol**,  $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot OH$ , Phenyl glycol, is obtained from styrolene dibromide,  $C_6H_5 \cdot CHBr \cdot CH_2Br$ ; it crystallizes from benzene, and benzene, in silky needles, melts at  $67-68^\circ$ , and can be sublimed. It is very soluble in water, alcohol and ether. Dilute nitric acid oxidizes it to benzoyl carbinol.

**Phenyl Methyl Glycol**,  $C_6H_5 \cdot CH(OH) \cdot CH(OH) \cdot CH_3$ , exists in two modifications,  $\alpha$  and  $\beta$ , like hydrobenzoin. These are obtained from phenyl dibromopropane,  $C_6H_5 \cdot CHBr \cdot CHBr \cdot CH_3$  (from propyl benzene). The  $\alpha$ -body melts at  $53^\circ$ , the  $\beta$ - at  $93^\circ$  (*Ber.*, 17, 709).

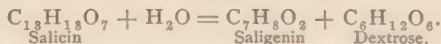


**Benzoyl Carbinol**,  $C_6H_5.CO.CH_2.OH$  (Acetophenone Alcohol), is a *Ketone* alcohol, formed from the bromide,  $C_6H_5.CO.CH_2.Br$ , by its conversion into acetate, and saponification with potassium carbonate (*Ber.*, 16, 1290). It crystallizes from water and alcohol in large, brilliant leaflets, which contain water of crystallization, and melt at  $73-74^\circ$ . It crystallizes from ether in shining anhydrous plates, and melts at  $85-86^\circ$ . When distilled it decomposes with formation of bitter almond oil. As it is a ketone, it affords crystalline compounds with primary alkaline sulphites. Like acetyl carbinol (p. 213), it reduces an ammoniacal silver or copper solution (forming benzaldehyde and benzoic acid), and is oxidized to mandelic acid (p. 214, *Ber.*, 14, 2100). Nitric acid oxidizes it to benzoyl-carboxylic acid,  $C_6H_5.CO.CO_2H$ . It yields cyanhydrin with  $CNH_3$ , which then affords  $\alpha$ -phenyl glyceric acid. Hydroxylamine converts it into the isonitroso-compound,  $C_6H_5.C(N.OH).CH_2.OH$ , melting at  $70^\circ$ .

The *acetate*,  $C_6H_5.CO.CH_2.O.C_2H_3O$ , forms rhombic plates, melting at  $49^\circ$ ; the *benzoate* melts at  $117^\circ$ ; both reduce an ammoniacal silver solution, even in the cold.

Saligenin, anisyl alcohol and vanilline alcohol, are mixed dihydroxy derivatives, being alcohols and phenols at the same time.

**Saligenin**,  $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown CH_2.OH \end{smallmatrix}$ , Ortho-oxybenzyl alcohol, is formed when sodium amalgam acts upon salicylic aldehyde, or in the decomposition of the glucoside salicin with dilute acids or ferments:—



It consists of pearly tables, dissolves in hot water, alcohol and ether, melts at  $82^\circ$  and sublimes near  $100^\circ$ . Lead acetate causes a white precipitate in its solutions, and ferric chloride produces a deep blue color in them. It yields salicylic acid when oxidized; hence belongs to the ortho-series.

*Salicin*,  $C_{13}H_{18}O_7$ , the glucoside of saligenin, occurs in the bark and leaves of willows and some poplars, from which it may be extracted with water. It forms shining crystals, which dissolve easily in hot water and alcohol, and melt at  $198^\circ$ . Nitric acid oxidizes it to *helicin*,  $3C_{13}H_{16}O_7 + 2H_2O$ . Small needles, difficultly soluble in water and melting at  $175^\circ$ . Sodium amalgam reduces helicin again to salicin. Ferments, alkalies and acids decompose it into salicylic aldehyde and glucoses. Helicin has been synthetically prepared from salicylic aldehyde and aceto-chlorhydrase (p. 385).

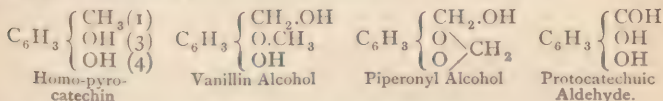
The glucoside, *Populin*,  $C_{20}H_{22}O_8$ , contained in several varieties of poplar, is the benzyl derivative of salicin,  $C_{13}H_{17}(C_7H_5O)O_7$ , and can be artificially made by the action of benzoyl chloride,  $C_7H_5OCl$ , or benzoic anhydride upon salicin. When boiled with lime water it yields salicin and benzoic acid. Populin crystallizes in small prisms containing 2 molecules  $H_2O$ , dissolves with difficulty in water and possesses a sweet taste.

*Meta-oxybenzyl Alcohol*,  $C_6H_4(OH).CH_2.OH$  (1, 3), is formed from meta-oxybenzoic acid by means of sodium amalgam. It melts at  $67^\circ$ , and boils at  $300^\circ$ . Ferric chloride colors it violet. It is oxidized to meta-oxybenzoic acid when fused with KOH (but not with chromic acid, p. 494).

*Para-oxybenzyl Alcohol* (1, 4), is produced by the action of sodium amalgam upon paraoxybenzaldehyde. It melts at  $197^\circ$ . Its methyl ether is the so-called

**Anisyl Alcohol**,  $C_6H_4(O.CH_3).CH_2.OH$  (1, 4), obtained from anisic aldehyde by alcoholic potassium hydroxide. It is but slightly soluble in water, crystallizes in needles, melts at  $25^\circ$ , and boils at  $259^\circ$ . It forms anisic aldehyde and acid when oxidized.

**Vanillin Alcohol**,  $C_8H_{10}O_3$ , and **Piperonyl Alcohol**,  $C_8H_8O_3$ , are formed from their aldehydes, vanillin and piperonal, by acting on the solution with sodium amalgam. They are derivatives of homo-pyro-catechin and creosol (p. 499), and stand in intimate relation to proto-catechuic aldehyde. Vanillin alcohol is the methyl-phenol ether, piperonyl alcohol the methylene-phenol ether of the as yet unobtained protocatechuic alcohol (see vanillin) :—



Vanillin alcohol crystallizes in colorless prisms, melts at  $103-105^\circ$ , and dissolves easily in hot water and alcohol. Piperonyl alcohol is difficultly soluble in water, appears in long prisms, and melts at  $51^\circ$ .

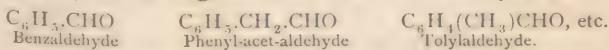
### TRIVALENT ALCOHOLS.

**Phenyl Glycerol** (Styicerine),  $C_9H_{12}O_3 = C_6H_5.CH(OH).CH(OH).CH_2.OH$ , is obtained from the bromide of cinnamic alcohol,  $C_6H_5.CHBr.CHBr.CH_2.OH$ , by long boiling with water. It is a gummy mass, easily soluble in water and alcohol.

**Mesitylene Glycerol**,  $C_6H_3(CH_2.OH)_3$ , is produced from tribrom-mesitylene,  $C_6H_3(CH_2Br)_3$  (melting at  $94^\circ$ ), upon boiling with water and lead carbonate. It is a thick liquid.

### ALDEHYDES.

The aldehydes of the benzene series, characterized by the group CHO, are perfectly analogous, as regards methods of formation and properties, with slight modifications, to those of the paraffin series. They are distinguished as *monovalent* aldehydes, like :—



and divalent or *dialdehydes*, like phthalic aldehyde,  $C_6H_4(CHO)_2$ . There exist also aldehydes of mixed function (p. 213), such as the *aldehyde-phenols* or *oxyaldehydes*,  $C_6H_4(OH).CHO$ , etc.

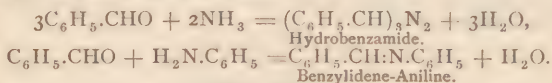
The monovalent aldehydes are obtained by the oxidation of the

corresponding primary alcohols, or by the distillation of the calcium salts of the aromatic acids with calcium formate (p. 148). They are derived from the benzene homologues by heating the halogen derivatives,  $C_6H_5.CHCl_2$ , with water, especially in the presence of bases (like sodium carbonate, lime, or lead oxide), or by boiling the mono-chlor-derivatives,  $C_6H_5.CH_2Cl$ , with water, in presence of oxidizing agents (lead nitrate).

A very interesting and direct conversion of homologous benzenes into aldehydes, is that occurring in the action of chromyl chloride,  $CrO_2Cl_2$ , and water (Etard).

Here the benzene homologues first unite (in  $CS_2$ -solution) with 2 molecules of chromyl chloride, forming brown pulverulent double-compounds, *e. g.*,  $C_6H_5.CH_3.(CrO_2Cl_2)_2$ , which yield aldehydes when added to water (*Ber.*, 17, 1462 and 1700). All the alkylic benzenes sustain this transformation; thus, from toluene,  $C_6H_5.CH_3$ , we obtain benzaldehyde,  $C_6H_5.CHO$ , from ethyl benzene,  $C_6H_5.CH_2.CH_3$ , phenyl acetaldehyde,  $C_6H_5.CH_2.CHO$ , from propylbenzene phenylpropyl aldehyde,  $C_6H_5.CH_2.CH_2.CHO$ . Tollyl aldehydes,  $C_6H_4(CH_3).CHO$ , are obtained from the xylenes, and from cymene tolyl-propyl aldehyde,  $C_6H_4(CH_3).CH_2.CH_2.CHO$ .

The benzaldehydes are mostly liquid bodies, difficultly soluble in water, possess an aromatic odor, and in deportment are very similar to the fatty aldehydes. They do not reduce alkaline copper (p. 150), but silver solutions with production of a metallic mirror. They differ from the fatty aldehydes in that they are, as a general thing, readily oxidized to alcohols and acids by alcoholic or aqueous alkalis (p. 507); it appears that this reaction is, however, only peculiar to those aldehydes in which the CHO-group is in direct union with the benzene nucleus. Furthermore, they do not directly combine with ammonia (p. 151), the amines and hydrazines, but yield compounds with them with immediate separation of water, and in the new derivatives all the amide hydrogen is replaced by the aldehyde radicals:—



Alcoholic potassium cyanide converts the benzaldehydes into benzoin (see these). Again, the benzaldehydes, like all benzene derivatives, readily furnish substitution products. An interesting fact is their ability to afford condensation products with the most heterogeneous bodies, water always disappearing (p. 155).

Thus, by condensation with the acids, aldehydes and ketones of the fatty series, we obtain unsaturated acids, aldehydes and ketones, *e. g.* :—



Occasionally an aldol condensation occurs here (p. 155), with formation of oxy-

bodies, *e. g.*,  $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$ , phenyl lactic acid, which give off water in addition. Such a condensation follows in consequence of the action of  $HCl$ -gas, zinc chloride, sulphuric acid and glacial acetic acid (*Ber.*, 14, 2460), or upon heating with acetic anhydride. The condensing influence (especially with acetone and acetaldehyde) of aqueous alkalis, *e. g.*, dilute sodium hydroxide and baryta water (*Ber.*, 14, 2468, and 15, 2856), is particularly interesting.

With malonic acid, the benzaldehydes form unsaturated dibasic acids, *e. g.*, benzal-malonic acid,  $C_6H_5 \cdot CH : C(CO_2H)_2$ , with acetacetic esters, acetyl carbonic acids, *e. g.*, benzal-acetacetic acid,  $C_6H_5 \cdot CH : C \begin{smallmatrix} \swarrow CO \cdot CH_3 \\ \searrow CO_2H \end{smallmatrix}$  (*Ann.*, 218, 121, and 223, 137). The benzaldehydes also condense with benzenes, phenols and anilines, forming derivatives of triphenyl methane ( $C_6H_5$ )<sub>3</sub>CH (see this).

## MONOVALENT ALDEHYDES.

1. **Benzaldehyde**,  $C_7H_6O = C_6H_5 \cdot CHO$ , **Bitter Almond Oil**, results from the oxidation of benzyl alcohol, and by the distillation of calcium benzoate and formate. Formerly it was prepared exclusively from its glucoside amygdalin (see below). At present it is made on a large scale from benzylic dichloride, with sulphuric acid, or by heating it under pressure with milk of lime, or by boiling benzyl chloride with water and lead nitrate. It is applied in the manufacture of benzoic and cinnamic acids, for preparing malachite green and other coloring substances.

The bitter-almond oil, prepared from chlorinated toluene, invariably contains chlorine; for its purification it is advisable to change it to its sodium bisulphite compound and then fractionate. Official bitter-almond oil is obtained from amygdalin; it usually contains hydrocyanic acid, which can be removed by shaking it with lime and ferrous chloride.

Bitter-almond oil is a colorless liquid with a pleasant odor, and high refractive power, and boils at  $179^\circ$ ; its specific gravity = 1.050 at  $15^\circ$ . It is soluble in 30 parts water, and is miscible with alcohol and ether. It shows all the reactions of the aldehydes; when oxidized (even in the air) it forms benzoic acid; by reduction (sodium amalgam) it passes into benzyl alcohol (together with hydrobenzoin). It affords crystalline compounds with the alkaline sulphites.  $CNH$  converts it into *Cyanhydrin*,  $C_6H_5 \cdot CH(OH) \cdot CN$  (mandelic nitrile) (p. 151)—a yellow oil, which solidifies on cooling.  $PCl_5$  converts it into benzal chloride,  $C_6H_5 \cdot CHCl_2$  (p. 425). Benzaldehyde dissolves in fuming sulphuric acid to form a crystalline sulphonic acid,  $C_6H_4(CHO) \cdot SO_3H$ , which affords salts, that crystallize well (*Ber.*, 16, 150).

A glucoside of benzaldehyde is *Amygdalin*,  $C_{20}H_{27}NO_{11}$ , occurring in the bitter almonds and in various plants, especially in the kernels of *Pomaceæ* and *Amygdalaceæ*, and the leaves of the cherry laurel. To obtain it the bitter almonds are freed of oil by pressing, and then digested with boiling alcohol, the solution is concentrated and the fatty oil removed with ether. Amygdalin crys-



tallizes from alcohol in white, shining leaflets; it tastes bitter, and dissolves readily in water and hot alcohol. It crystallizes from water in prisms, containing  $3\text{H}_2\text{O}$ . It yields a heptacetate when gently warmed with acetic anhydride. On boiling with dilute acids, or upon standing with water and *emulsin*, a ferment present in bitter almonds, amygdalin, is decomposed into oil of bitter almonds, dextrose and hydrocyanic acid:—



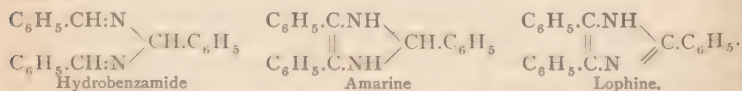
When amygdalin is boiled with alkalis, the nitrogen is evolved as ammonia and *amygdalic acid*,  $\text{C}_{20}\text{H}_{28}\text{O}_{13}$ , produced, which decomposes into mandelic acid and glucoses, when boiled with dilute acids.

### AMIDE DERIVATIVES OF BENZALDEHYDE.

The action of ammonia upon benzaldehyde or benzyldichloride,  $\text{C}_6\text{H}_5\cdot\text{CHCl}_2$  (p. 512), produces **Tribenzylene-diamine**,  $\text{C}_{21}\text{H}_{18}\text{N}_2 = (\text{C}_6\text{H}_5\cdot\text{CH})_3\text{N}_2$ , or **Hydrobenzamide**, which crystallizes from alcohol and ether in rhombic octahedra, melting at  $110^\circ$ . It reacts neutral, and does not combine with acids; but as a tertiary diamine it forms with ethyl iodide a *Diammonium Iodide*,  $\text{C}_{21}\text{H}_{18}\text{N}_2(\text{C}_2\text{H}_5\text{I})_2$ , which affords the *ammonium oxide*,  $\text{C}_{21}\text{H}_{18}\text{N}_2(\text{C}_2\text{H}_5)_2\text{O}$ , with silver oxide; this yields crystalline salts with two equivalents of the acids.

When hydrobenzamide is boiled with alcohol or acids oil of bitter almonds and ammonia result. Heated to  $120^\circ$  or boiled with caustic potash it changes to isomeric **amarine**,  $\text{C}_{21}\text{H}_{16}\text{N}_2$ , which crystallizes from alcohol and ether in prisms, melting at  $113^\circ$ . It reacts (in alcoholic solution) alkaline, and with one equivalent of the acids yields salts which are difficultly soluble in water. When amarine or hydrobenzamide is subjected to distillation, or if the former be oxidized with  $\text{CrO}_3$  (in glacial acetic acid) we obtain **Lophine**,  $\text{C}_{21}\text{H}_{16}\text{N}_2$ , which can also be prepared from cyanphenine,  $(\text{C}_6\text{H}_5\cdot\text{CN})_3$ , by the action of nascent hydrogen (with disengagement of  $\text{NH}_3$ ) (*Ber.*, 15, 1493). It is not readily soluble in alcohol, crystallizes in long needles, and melts at  $275^\circ$ . It yields crystalline salts with one equivalent of the acids. It exhibits the property of phosphorescing in marked degree when shaken with alcoholic potash; it is then decomposed into  $\text{NH}_3$  and benzoic acid (p. 150).

The constitution of these compounds is probably represented in the following formulas:—



Hence lophine possesses a structure analogous to the glyoxalins (p. 279) and the anhydro-bases (p. 455) (*Ber.*, 15, 2410, 2333). It is prepared synthetically by acting with ammonia upon an alcoholic solution of benzil,  $\text{C}_6\text{H}_5\cdot\text{CO}$ , with

benzaldehyde (*Ber.*, 15, 1493, 2412) in the same manner as glyoxalethylins are obtained from glyoxal with aldehydes (p. 280). An oxy-lophine,  $\text{C}_{21}\text{H}_{15}(\text{OH})\text{N}_2$ , is obtained from para-oxybenzaldehyde. When distilled with zinc dust it yields lophine. The latter, like the glyoxalins, does not form an acetate. Amarine affords dialkyl derivatives when it is heated with alkyl iodides, whereas with lophine the mono-alkyl compounds only result; and these unite with alkyl

iodides to yield ammonium iodides, *e. g.*,  $C_{21}H_{15}(CH_3)_2N_2 \cdot CH_3I$  (*Ber.*, 15, 2333, and 16, 1272).

When benzaldehyde is digested with aniline it becomes **Benzylidene Aniline**,  $C_6H_5 \cdot CH:N \cdot C_6H_5$ , which crystallizes in yellow needles melting at  $41^\circ$ . Acids decompose it on warming into its components. Similarly, we obtain from benzaldehyde and ortho-toluidine **Benzylidene Toluidine**,  $C_6H_5 \cdot CH:N \cdot C_6H_4(CH_3)$ ; when the latter is distilled with zinc dust we obtain methylphenanthridine (*Ber.*, 15 2917).

When benzaldehyde unites with the amides, *e. g.*,  $C_2H_5O \cdot NH_2$ , not only is all the amid-hydrogen (p. 512) eliminated, but two molecules of the amides are combined.

The *aldehydine bases* resulting from the combination of benzaldehyde with ortho-phenylene diamines have already received mention (p. 455).

The benzaldehydes unite also with phenyl-hydrazines, *e. g.*,  $C_6H_5 \cdot NH \cdot NH_2$  (even in dilute aqueous solution), forming crystalline compounds (p. 152), which serve for the recognition of the aldehydes (*Ber.*, 17, 574).

**Benzylidene-Phenyl-Hydrazine**,  $C_6H_5 \cdot CH:N \cdot NH \cdot C_6H_5$ , crystallizes from alcohol, melts at  $152.5^\circ$ , and distils. It reduces Fehling's solution, and decomposes on heating with acids into benzaldehyde and phenylhydrazine.

The benzaldehydes form aldoxims (p. 152) with hydroxylamine. **Benzal-doxim**,  $C_6H_5 \cdot CH:N(OH)$ , is a colorless oil, boiling above  $220^\circ$ . When boiled with acids it splits up into  $NH_2 \cdot OH$  and benzaldehyde. Alkyl ethers (*Ber.*, 16, 824) are produced when the alkyl iodides act on the sodium salt.

## SUBSTITUTION PRODUCTS OF BENZALDEHYDE.

The halogen benzaldehydes are obtained by substituting the nucleus of the benzyl chlorides  $C_6H_5 \cdot CH_2Cl$  and  $C_6H_5 \cdot CHCl_2$ . They result from the latter by the action of chlorine in the presence of iodine, when the para-position is replaced. Benzoyl chloride,  $C_6H_5 \cdot COCl$ , results on leading chlorine into boiling benzaldehyde; hence the latter acts like toluene in chlorination (p. 420).

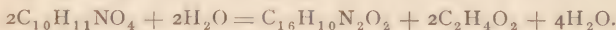
## NITROBENZALDEHYDES.

On dissolving benzaldehyde in nitric-sulphuric acid, or in a mixture of sulphuric acid with nitre (calculated amount) below  $30-35^\circ$ , the chief product is meta-nitrobenzaldehyde, which separates in a crystalline form. The oil (20-25 per cent.) consists principally of ortho-nitrobenzaldehyde, which cannot, however, be well obtained in pure form (*Ber.*, 14, 2802). Ortho-nitrobenzaldehyde is obtained pure from ortho-nitrobenzaloxim (see below), when it is oxidized with a chromic acid mixture (*Ber.*, 14, 2334); also from ortho-nitrocinnamic ester, through the action of nitric acid and sodium nitrite (*Ber.*, 14, 2803). *It is best obtained from ortho-nitro-cinnamic acid*, by oxidizing the alkaline solution with potassium permanganate in the presence of benzene (*Ber.*, 17, 121.)

**Ortho-nitro-benzaldehyde**,  $C_6H_4(NO_2) \cdot CHO$ , dissolves easily in alcohol and ether, but slightly in water, from which it crystallizes in long, yellowish needles. It melts at  $46^\circ$ , and distils with scarcely any decomposition. It possesses a peculiar odor, which is penetrating in the heat, and it distils with aqueous vapor.  $MnO_4K$ , or chromic acid, oxidizes it to ortho-nitrobenzoic acid; with concen-

trated sodium hydroxide ortho-nitrobenzal alcohol and ortho-nitrobenzoic acid are readily produced.

o-Nitro-benzaldehyde condenses with acetone (under the influence of a very little sodium hydroxide or baryta water (p. 513) to ortho-nitro-phenyl-lactic-methyl-ketone,  $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$ , which with more caustic soda immediately splits off acetic acid and *indigo* (*Ber.*, 15, 2856):—



It condenses in the same manner with acetaldehyde to ortho-nitro-phenyl-lactic aldehyde,  $C_6H_4(NO_2).CH(OH).CH_2.CHO$ , and ortho-nitrophenyl-cinnamic aldehyde,  $C_6H_4(NO_2).CH:CH.CHO$  (p. 155). The first of these also forms indigo with the alkalis.

With hydroxylamine, ortho-nitro-benzaldehyde yields the *aldoxim*,  $C_6H_4(NO_2).CH(N.OH)$ , melting at  $95^\circ$ . It results also from ortho-nitro-para-amidophenyl acetic acid by the action of nitrous acid, and then boiling with alcohol. It has been called nitroso-methyl-ortho-nitrobenzene (*Ber.*, 15, 3057). Heated with hydrochloric acid, it is split up into  $NH_3$  and ortho-nitrobenzoic acid; when oxidized (ferric chloride) it forms ortho-nitrobenzaldehyde with evolution of hyponitrous oxide.

**Meta-nitro-benzaldehyde**,  $C_6H_4(NO_2).CHO$  (1, 3), results from the nitration of benzaldehyde (see above). It crystallizes from water in white needles, melting at  $58^\circ$ . When reduced it yields meta-amidobenzaldehyde, and when oxidized meta-nitrobenzoic acid.  $PCl_5$  and reduction convert it into metatoluidine. Its *aldoxim*,  $C_6H_4(NO_2).CH(N.OH)$ , melts at  $119^\circ$ , and is identical with the so-called nitroso-methyl-meta-nitro benzene (*Ber.*, 15, 838 and 3060), obtained from meta-nitro-para-amidophenyl acetic acid. Ferric chloride decomposes it into  $N_2O$  and meta nitrobenzaldehyde (*Ber.*, 15, 2004).

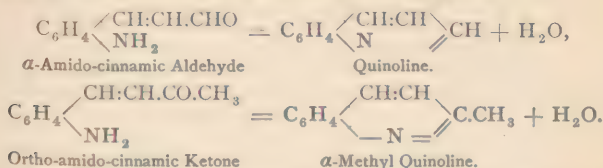
**Para-nitro-benzaldehyde**,  $C_6H_4(NO_2).CHO$  (1, 4), results when para-nitrobenzyl chloride,  $C_6H_4(NO_2).CH_2Cl$ , is boiled with water and lead nitrate, or when sulphuric acid acts upon para-nitrobenzal chloride,  $C_6H_4(NO_2).CHCl_2$  (*Ber.*, 16, 2539); finally, by the oxidation of para-nitrocinnamic acid with sulphuric acid and nitre (*Ber.*, 16, 2714). It crystallizes from water in thin prisms, and melts at  $106^\circ$ . Its *aldoxim*,  $C_6H_4(NO_2).CH(N.OH)$ , melts at  $128^\circ$ , and decomposes into  $NH_2.OH$  and para-nitrobenzaldehyde (*Ber.*, 16, 2003), when digested with acids.

#### AMIDOBENZALDEHYDES.

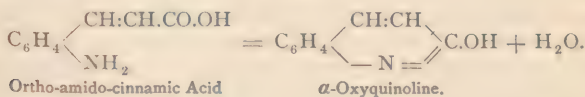
These are obtained by the reduction of the nitrobenzaldehydes.

**Ortho-amido-benzaldehyde**,  $C_6H_4(NH_2).CHO$  (1, 2), is best obtained by reducing ortho-nitrobenzaldehyde with ferrous sulphate and ammonia (*Ber.*, 17, 456). It is difficultly soluble in water, from which it crystallizes in silvery leaflets, melting at  $40^\circ$  to a yellowish oil. It possesses an intense odor, and volatilizes very readily in steam. It reduces an ammoniacal silver solution. Nitrous acid converts it into salicylic aldehyde. Its *aldoxim*,  $C_6H_4(NH_2).CH(N.OH)$ , results by the reduction of ortho-nitrobenzal-doxim with ammonium sulphide. It melts at  $133^\circ$ , and when oxidized with  $FeCl_3$ , splits up into  $N_2O$  and ortho-amido-benzaldehyde (*Ber.*, 15, 2004).

Ortho-amido-benzaldehyde yields condensation products with aldehydes, ketones, and acids of the fatty series (p. 512). By the withdrawal of water (and inner condensation) these new compounds pass into quinoline derivatives (*Ber.*, 16, 1833):—



$\alpha$ -Oxyquinoline (carbostyrl) is produced by condensation with acetic anhydride and sodium acetate:—



With malonic acid it yields  $\alpha$ -oxyquinoline carboxylic acid (*Ber.*, 17, 456).

**Meta-amido-benzaldehyde**,  $\text{C}_6\text{H}_4(\text{NH}_2).\text{CHO}$  (1, 3), has not been obtained in a pure condition. It results in the reduction of meta-nitrobenzaldehyde with stannous chloride or ferrous sulphate and ammonia; also by oxidizing its aldoxim with ferric chloride (*Ber.*, 15, 2044, and 16, 1997). By diazotizing it yields meta-oxybenzaldehyde. Its aldoxim,  $\text{C}_6\text{H}_4(\text{NH}_2).\text{CH}(\text{N.OH})$ , is obtained by the reduction of meta-nitrobenzalaldoxim with ferrous sulphate and ammonia. It melts at 88°.

**Para-amido-benzaldehyde**,  $\text{C}_6\text{H}_4(\text{NH}_2).\text{CHO}$  (1, 4), is obtained from its aldoxim through the agency of acids. It crystallizes from water in leaflets, melting at 71°; these are not very stable. Its aldoxim,  $\text{C}_6\text{H}_4(\text{NH}_2).\text{CH}(\text{N.OH})$ , is afforded by the reduction of para-nitrobenzalaldoxim. It melts at 124–129° (*Ber.*, 16, 2001).

## 2. Toluic Aldehydes, $\text{C}_6\text{H}_4(\text{CH}_3).\text{CHO}$ .

These can be easily obtained from the three xylenes,  $\text{C}_6\text{H}_4(\text{CH}_3)_2$ , through the action of  $\text{CrO}_2\text{Cl}_2$  and water (p. 512). (*Ber.*, 17, 1464). The ortho- and meta-bodies resemble bitter-almonds in odor.

*o*-Toluic Aldehyde results from ortho-xylene chloride,  $\text{C}_6\text{H}_4(\text{CH}_3).\text{CH}_2\text{Cl}$ . It boils at 200°, and readily oxidizes, on exposure to the air, to ortho-toluic acid.

*m*-Toluic Aldehyde, obtained from meta-xylene chloride, boils at 199°, and when exposed soon oxidizes to meta-toluic acid. When nitrated it yields an ortho-nitro-aldehyde; this forms *methyl indigo* (*Ber.*, 16, 817; 17, 1473) with acetone and caustic soda.

*p*-Toluic Aldehyde is obtained by the distillation of calcium paratoluate and formate. Its odor resembles that of peppermint; it boils at 204°, and is easily oxidized to para-toluic acid.

The so-called  $\alpha$ -Toluic Aldehyde,  $\text{C}_6\text{H}_5.\text{CH}_2.\text{CHO}$ , Phenylacetaldehyde, is produced when chromyl chloride and water act upon ethyl benzene,  $\text{C}_6\text{H}_5.\text{C}_2\text{H}_5$ ; by distillation of  $\alpha$ -toluate of calcium and calcium formate; by heating  $\beta$ -phenyl-lactic acid or phenyl-oxy-acrylic acid with dilute sulphuric acid; from



so-called phenyl- $\alpha$ -chlor-lactic acid,  $C_6H_5 \cdot CH(OH) \cdot CHCl \cdot CO_2H$ , by the action of sodium hydroxide (*Ber.*, **16**, 1286); or from phenyl- $\alpha$ -brom-lactic acid,  $C_6H_5 \cdot CH(OH) \cdot CHBr \cdot CO_2H$ , with a soda solution (*Ann.*, **219**, 179), and, finally, by acting with water on  $\alpha$ -bromstyrolene. It is an oil, boiling at  $206^\circ$ , and yielding benzoic acid upon oxidation with nitric acid.  $PCl_5$  converts it into  $\alpha$ -dichlor-ethyl benzene,  $C_6H_5 \cdot CH_2 \cdot CHCl_2$  (p. 416). Nitration converts it into a compound which affords indol,  $C_8H_7N$ , when reduced or heated with zinc dust (*Ber.*, **17**, 984). By the action of chloral and  $AlCl_3$  upon benzene there is obtained the **Phenyldichloroacetaldehyde**,  $C_6H_5 \cdot CCl_2 \cdot CHO$ , which reduces Fehling's and silver nitrate solutions, and oxidizes easily to the acid,  $C_6H_5 \cdot CCl_2 \cdot CO_2H$  (*Ber.*, **17**, Ref. 229).

3. **Phenyl-propyl Aldehyde**,  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CHO$ , hydrocinnamic aldehyde, results from propyl benzene by means of chromyl chloride. It boils at  $208^\circ$ .

#### 4. Aldehydes, $C_{10}H_{12}O$ .

**Cumic Aldehyde**,  $C_6H_4(C_3H_7) \cdot CHO$ , **Cuminol**, is the isopropyl-benzaldehyde of the para-series. It occurs together with cymene,  $C_{10}H_{14}$ , in Roman caraway oil, and in oil of *Cicuta virosa*, or water hemlock, etc. In order to effect its separation shake the oil, boiling above  $190^\circ$ , with hydric sodic sulphite, press out the separated crystalline mass, and decompose it by distillation with sodium carbonate. Cuminol possesses an aromatic odor, has a specific gravity = 0.973 at  $13^\circ$ , and boils at  $235^\circ$ . Dilute nitric acid oxidizes it to cumic acid; chromic acid converts it into terephthalic acid. When distilled with zinc dust, the isopropyl group is transposed and ordinary cymene results.

*Nitro-Cuminol*,  $C_6H_3(NO_2)(C_3H_7) \cdot CHO$ , melts at  $54^\circ$ , and when acted upon by  $PCl_5$ , reduced, etc., yields thymol (p. 494).

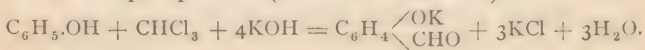
**p-Methyl Phenyl-Propyl Aldehyde**,  $C_6H_4(CH_3) \cdot CH_2 \cdot CH_2 \cdot CHO$ , is obtained from common cymene with chromyl chloride. It is an oil boiling at  $220^\circ$ , and oxidized by dilute nitric acid to paratoluic acid,  $C_6H_4(CH_3) \cdot CO_2H$  (*Ber.*, **17**, 1931).

**Paraphthalyl Aldehyde**,  $C_6H_4(CHO)_2$  (1, 4), is a bivalent aldehyde, corresponding to tolylene alcohol (p. 509). It is obtained from tolylene chloride,  $C_6H_4(CH_2Cl)_2$ , on heating it with water and lead nitrate. Needles difficultly soluble in water and melting at  $115^\circ$ . When oxidized it affords terephthalic acid.

The supposed ortho-phthalyl aldehyde, from ortho-phthalyl chloride,  $C_6H_4(COCl)_2$ , is phthalid (see this).

### ALDEHYDE-PHENOLS OR OXY-ALDEHYDES.

The oxy-aldehydes, having hydroxyl in the benzene nucleus, are obtained by oxidizing (p. 510) the oxy-alcohols with chromic acid. An important synthetic method, wherein the aldehyde group is directly introduced, consists in letting chloroform and an alkaline hydroxide act upon phenols (reaction of Reimer):—



All the benzene oxy-derivatives (the oxyacids also) react similarly; hence innumerable oxy-aldehydes have been prepared.

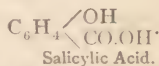
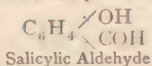
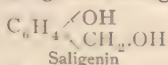
To perform the reaction, dissolve the phenol and some potassium or sodium hydroxide in 1½–2 parts water, and while heating on a water bath, in connection with a return condenser, gradually add chloroform. Choral can be substituted for the latter. The excess of chloroform is distilled off, the residue supersaturated with hydrochloric or sulphuric acid, and the separated aldehyde finally extracted with ether. Ortho-formic phenyl ether is produced at the same time (p. 483).

It is very probable the reaction proceeds in such a manner that formic acid first results from the action of the alkali on chloroform:  $\text{CHCl}_3 + 4\text{KOH} = \text{CHO} \cdot \text{OK} + 3\text{KCl} + 2\text{H}_2\text{O}$  (p. 173) and as it is produced, acts on the phenol. Oxyacids are obtained in the same way, when  $\text{CCl}_4$  is employed. In this reaction, very frequently the  $\text{CO}_2\text{H}$ -group, occupying the para-position in the oxyacids (para-oxy-benzoic acid), is exchanged for  $\text{CHO}$  (Ber., 9, 1268).

In deportment the oxaldehydes are perfectly analogous to the monovalent benzaldehydes. They reduce an ammoniacal silver solution, but not the Fehling solution. Oxidizing agents convert them with difficulty into oxyacids; this is most easily accomplished by fusion with caustic alkalis. They dissolve in alkalis, forming salts, e. g.,  $\text{C}_6\text{H}_4(\text{CHO})\cdot\text{ONa}$ ; the alkyl iodides convert the latter into alkyl ethers (p. 480). They give aldoxims with hydroxylamine.

#### 1. Oxybenzaldehydes, $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CHO}$ .

**Ortho-oxybenzaldehyde** (1, 2), **Salicylic Aldehyde**, occurs in the volatile oils of the different varieties of *Spiræa*. It is obtained by the oxidation of saligenin and salicin (p. 510), but is most readily prepared (together with para-oxybenzaldehyde) by the action of chloroform and caustic potash upon phenol (Ber., 10, 213). An oil with an aromatic odor; solidifies at  $20^\circ$ , and boils at  $196^\circ$ ; its specific gravity = 1.172 at  $15^\circ$ . It volatilizes readily with steam. It is rather easily soluble in water; the solution is colored a deep violet by ferric chloride. It colors the skin an intense yellow. Sodium amalgam transforms it into saligenin; oxidizing agents change it to salicylic acid:—



Salicylic aldehyde dissolves in caustic potash to form the crystalline derivative,  $\text{C}_6\text{H}_4(\text{OK})\text{CHO}$ , from which ethers are obtained through the agency of alkyl iodides. The methyl ether,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_3)\cdot\text{CHO}$ , melts at  $35^\circ$ , and boils at  $238^\circ$ ; the ethyl ether boils at  $248^\circ$ . Salicyl aldoxim melts at  $57^\circ$ .

**Meta-oxybenzaldehyde** (1, 3) results together with the alcohol in the reduction of meta oxybenzoic acid with sodium amalgam, and from meta nitrobenzaldehyde by reduction and diazotizing (Ber., 15, 2044). It crystallizes from hot water in white needles, melts at  $104^\circ$ , and boils near to  $240^\circ$ . By nitration it yields two mononitro-bodies,  $\alpha$  and  $\beta$  (the so-called  $\gamma$  compound is a mixture of  $\alpha$  and  $\beta$ ), which melt at  $128^\circ$  and  $166^\circ$  respectively. Their methyl ethers,  $\text{C}_6\text{H}_3(\text{NO}_2)(\text{CHO})(\text{O}\cdot\text{CH}_3)$ , melt at  $107^\circ$  and  $83^\circ$ . The  $\alpha$ -methyl ether (containing the nitro-group in the para position) affords vanillin by the replacement of  $\text{NO}_2$  with  $\text{OH}$ ; the  $\beta$ -methyl ether ( $\text{NO}_2$  in ortho-position) yields a dye similar to indigo when treated with acetone and caustic potash (Ber., 15, 2052, 3056, 17, 1381).

**Para-oxybenzaldehyde** is formed from phenol, together with salicylic aldehyde; also by the reduction of para-oxybenzoic acid, and by heating anisic aldehyde to  $200^{\circ}$  with hydrochloric acid. It is rather easily soluble in hot water, crystallizes in small needles, melts at  $116^{\circ}$ , and sublimes. Ferric chloride colors it the same as phenol. It yields para-oxybenzoic acid on fusion with KOH. Its aldoxim melts at  $65^{\circ}$ . Its methyl ether is the so-called—

**Anisic Aldehyde**,  $C_6H_4(O.CH_3).CHO$ , which results in oxidizing various essential oils (anise, fennel, etc.) with dilute nitric acid, or a chromic acid mixture. A soda solution will liberate it from its crystalline compound with sodium bisulphite. It is a colorless oil of specific gravity 1.123 at  $15^{\circ}$ , and boils at  $248^{\circ}$ .

The substance in the oils, which affords the aldehyde by oxidation, is *anethol*,  $C_{10}H_{12}O$ , the methyl ether of *anol*. When the oils (anise, fennel) are cooled, anethol crystallizes in white, glistening scales, which melt at  $21^{\circ}$ , and boil at  $232^{\circ}$ . Anethol is obtained synthetically from methyl-paraoxy-phenyl crotonic acid (*Ber.*, 10, 1604). When oxidized with chromic acid it splits into acetic and anisic acids. Heated with HI, the methyl group is eliminated and the mass resinified. Fused with caustic potash anethol becomes so-called *anol*,  $C_6H_4(OH).CH:CH.CH_3$ . The latter consists of shining leaflets, melting at  $92^{\circ}$ , and distilling with decomposition.

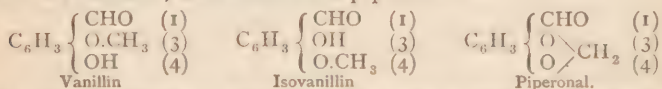
2. **Dioxybenzaldehydes**,  $C_7H_6O_3 = C_6H_3(OH)_2.CHO$ .

Three of the six possible isomerides have been prepared from the dioxybenzenes,  $C_6H_4(OH)_2$ , by means of the chloroform reaction; likewise, six methyl dioxybenzaldehydes,  $C_6H_3(O.CH_3).(OH).CHO$ , have been obtained from the three mono-methyl-dioxybenzenes (*Ber.*, 14, 2024). Dialdehydes also are simultaneously produced in dilute solutions when  $CCl_3H$  and KOH are employed.

**$\beta$ -Resorcylic Aldehyde**,  $C_6H_3(OH)(OH).CHO$  (1, 3, 4), obtained from resorcinol, melts at  $135^{\circ}$ , and with acetic anhydride yields (according to Perkin) umbelliferon. **Gentisin Aldehyde**,  $C_6H_3(OH)(OH).CHO$  (1, 4, CHO), from hydroquinone, melts at  $99^{\circ}$ , and affords gentisinic acid on oxidation.

**Protocatechuic Aldehyde**,  $C_6H_3(OH)(OH).CHO$  (1, 3, 4 —CHO in 1), the parent substance of vanillin and piperonal, was first obtained from the latter; it is prepared synthetically from pyrocatechin by the chloroform reaction (*Ber.*, 14, 2015); also by heating its ethers, vanillin, isovanillin and piperonal, with dilute hydrochloric acid to  $200^{\circ}$ , and from opianic acid. It dissolves readily in water, forms brilliant crystals (from toluene), and melts at  $150^{\circ}$ . It reduces silver solutions with the production of a mirror, and combines with alkaline bisulphites. Ferric chloride colors its aqueous solution deep green (p. 496).

Protocatechuic aldehyde is a derivative of homopyrocatechin (p. 499); its acid is protocatechuic acid (see this). Its important ethers are vanillin, isovanillin and piperonal:—



The two OH groups in protocatechuic aldehyde occupy the ortho-position, but the CHO group the para with reference to one of the OH groups (see protocatechuic acid). For the position of the methyl group in vanillin see *Ber.*, 9, 1283, and 11, 125; it is intimately related to creosol (p. 500).

**Vanillin**,  $C_8H_8O_3$ , methyl protocatechuic aldehyde, is the active and odorous constituent of the vanilla bean pods (about two per cent.). It was first prepared artificially from the glucoside coniferine, by its oxidation with chromic acid (Tiemann), a procedure now applied technically for the obtainment of vanillin. It is formed synthetically, together with an isomeric aldehyde, when guaiacol is acted upon by chloroform and caustic alkali (*Ber.*, **14**, 2021), also from the methyl ether of  $\alpha$ -nitro-metaoxy-benzaldehyde (p. 519), and by oxidizing eugenol and clove-oil.

*Coniferine*,  $C_{16}H_{22}O_8 + 2H_2O$ , is found in the cambium of coniferous woods, and consists of shining needles. It effloresces in the air, and melts at  $185^\circ$ . It acquires a dark blue color when moistened with phenol and hydrochloric acid. Boiling acids or emulsin decompose it into glucoses and *Coniferyl Alcohol*,  $C_{10}H_{12}O_3 = C_6H_5\left(\frac{O.CH_3}{OH}\right).C_3H_4.OH$ ; the latter melts at  $75^\circ$ , and is oxidized to vanillin (together with homovanillin) by chromic acid.

Vanillin crystallizes in stellate groups of needles, is soluble in hot water, alcohol and ether, melts at  $80-81^\circ$ , and sublimes. As a phenol it affords salts with one equivalent of a base; as an aldehyde it combines with primary alkaline sulphites. Heated with  $HCl$  to  $180^\circ$  it decomposes into  $CH_3Cl$  and protocatechuic aldehyde. Protocatechuic acid results on fusion with potassium hydroxide (the aldehyde group is oxidized and methyl split off). Nascent hydrogen converts vanillin into vanillin alcohol (p. 511); energetic oxidation carries it to vanillinic acid.

Isovanillin (see above) is obtained by oxidizing hesperitinic acid or by heating opianic methyl ether with hydrochloric acid.

*Dimethylprotocatechuic Aldehyde*,  $C_6H_5(O.CH_3)_2CHO$  Methylvanillin, is obtained from vanillin by the action of methyl iodide and potassium hydroxide. It is difficultly soluble in water, melts about  $20^\circ$ , and boils near  $285^\circ$ . It yields dimethylprotocatechuic acid by oxidation.

**Piperonal**,  $C_8H_8O_3$ , obtained by oxidizing piperic acid (see this), is the methylene ether of protocatechuic aldehyde (p. 520). It consists of crystals which are difficultly soluble in water, melt at  $37^\circ$ , and boil at  $263^\circ$ . Being an aldehyde it unites with primary alkaline sulphites. When oxidized it affords piperonylic acid, when reduced piperonyl alcohol (p. 511).

$PCl_5$  converts it into the chloride,  $C_6H_5(O_2.CCl_2)CHCl_2$ , which yields protocatechuic aldehyde when boiled with water; the group  $CCl_2$  splits off.

## KETONES.

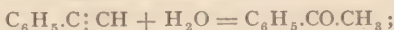
The ketones in which two benzene nuclei are joined by the ketonic group  $CO$ , *e. g.*, benzophenone,  $C_6H_5.CO.C_6H_5$ , will receive attention later. At this point we will only consider the so-called *mixed* ketones, containing a benzene and also an alkyl group:—

$C_6H_5.CO.CH_3$ , Acetophenone.

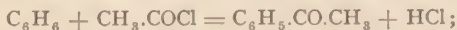
These are perfectly analogous to the ketones of the paraffin series,



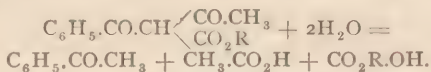
and are obtained by similar methods, chiefly by the distillation of a mixture of calcium salts of an aromatic and a fatty acid (p. 148). They also result when sulphuric acid (diluted  $\frac{1}{2}$  volume) acts on the phenylacetylenes (pp. 61 and 162):—



or from the benzenes on boiling with fatty acid chlorides and  $\text{AlCl}_3$ :—



and by the decomposition of benzoyl acetic esters (p. 222) when they are boiled with water or sulphuric acid (30 per cent.) (*Ber.*, 15, 2084);—



Benzoyl acetones (diketones) are produced at the same time as intermediate products (in slight amount), *e. g.*,  $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_2.\text{CO}.\text{CH}_3$ . They dissolve in alkalis, and are precipitated by  $\text{CO}_2$ . The nitro-benzoyl aceto-acetic esters deport themselves similarly (*Ber.*, 16, 2239; *Ann.*, 221, 332). Thus from acetophenone-bromide,  $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_2\text{Br}$ , we obtain bodies with aceto-acetic esters, from which, by decomposition, the diketones of the type  $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_2.\text{CH}_2.\text{CO}.\text{CH}_3$ , are obtained (*Ber.*, 17, 68 and 913); these are insoluble in alkalis.

The benzene ketones are oils, insoluble in water, and boil without decomposition; phenyl methyl ketone is the only one that is a solid. With the exception of benzyl-methyl ketone they do not unite with alkaline bisulphites. Nascent hydrogen converts them into secondary alcohols which form ketones when oxidized. Chromic acid transforms the ketones  $\text{C}_6\text{H}_5.\text{COR}$  into benzoic acid and the alkyl, which is further oxidized (p. 162). All ketones yield *acetoxims* with hydroxylamine; they combine, too, in the same way with phenylhydrazine (p. 161).

**Phenyl-methyl-ketone**,  $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_3$ , Acetophenone, results by the action of zinc methyl on benzoyl chloride,  $\text{C}_6\text{H}_5.\text{COCl}$ , and is obtained by distilling benzoate (100 parts) of calcium with calcium acetate (56 parts).

The most convenient method consists in boiling benzene (10 parts) with acetyl chloride (1 part) and  $\text{AlCl}_3$  (2 parts). It crystallizes in large plates, melts at  $20.5^\circ$ , and boils at  $200^\circ$ . Nascent hydrogen converts it into phenyl-ethyl alcohol (p. 508); chromic acid oxidizes it to  $\text{CO}_2$  and benzoic acid. Its *acetoxim*,  $\text{C}_6\text{H}_5.\text{C}(\text{N.OH}).\text{CH}_3$ , melts at  $59^\circ$ ; the phenyl-hydrazine,  $\text{C}_6\text{H}_5.\text{CH}_3.\text{C}:\text{N.NH}.\text{C}_6\text{H}_5$ , at  $105^\circ$ . Acetophenone affords  $\beta$ -dichlorethyl benzene with  $\text{PCl}_5$  (p. 416); with  $\text{CNH}$  and hydrochloric acid atrolactic acid.

The chlorination of boiling acetophenone produces the so-called **Acetophenone Chloride**,  $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_2\text{Cl}$ , melting at  $59^\circ$ , and boiling at  $245^\circ$ . The *bromide*,  $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_2\text{Br}$ , results in the action of bromine on acetophenone (100 gr. with

500 grs. glacial acetic acid, and 134 grs. bromine, *Ber.*, 15, 2464). It crystallizes in large, rhombic prisms, melting at  $50^{\circ}$ ; its vapors provoke tears. Sodium acetate converts it into the acetic ester, which is saponified to benzoyl carbinol (p. 510). Hydroxylamine affords the body  $C_6H_5.C(N.OH).CH_2.HN.OH$ , melting at  $163^{\circ}$ ; acetophenone dibromide,  $C_6H_5.CO.CHBr_2$ , yields *Phenylglyoxim*,  $C_6H_5.C(N.OH).CH(N.OH)$ , (p. 164), melting at  $152^{\circ}$  (*Ber.*, 16, 2186).

Ammonia converts the chloride or bromide into *isoindol*,  $C_{16}H_{14}N_2$  (*Ber.*, 16, 342).

**Nitro-acetophenones**,  $C_6H_4(NO_2).CO.CH_3$ .

The meta-body is the chief product (just as in the case of benzaldehyde) when acetophenone is dissolved in cold, fuming nitric acid. An isomeric oil is formed at the same time. The three isomerides can be prepared from the three nitrobenzoyl-aceto-acetic esters, which result from the action of the nitrobenzoyl chlorides,  $C_6H_4(NO_2).COCl$ , upon aceto-acetic esters (p. 522).

**o-Nitroacetophenone** is a yellowish oil, of peculiar odor, and does not solidify on cooling. Bromine converts it into a mono- and a dibromide, from which indigo is obtained by action of ammonium sulphide (*Ann.*, 221, 330). **Nitroacetophenone** crystallizes in needles, melts at  $93^{\circ}$ , volatilizes with steam, and is oxidized to meta-nitrobenzoic acid by potassium permanganate. **Para-Nitroacetophenone** results on digesting para-nitrophenyl-propionic acid,  $C_6H_4(NO_2).C:C.CO_2H$ , with sulphuric acid; it first parts with  $CO_2$  and the resulting nitrophenyl-acetylene,  $(C_6H_4(NO_2).C:CH)$ , absorbs water (p. 522). Para-nitroacetophenone forms yellowish prisms, melts at  $80^{\circ}$ , and with  $PCl_5$  yields para-nitrochlorostyrol,  $C_6H_4(NO_2).CCl:CH_2$  (*Ann.*, 212, 159).

**Amido-acetophenones**,  $C_6H_4(NH_2).CO.CH_3$ .

**o-Amido-acetophenone** (1, 2) is obtained: by reducing ortho-nitroacetophenone with tin and hydrochloric acid; from ortho-amido-phenyl acetylene,  $C_6H_4(NH_2).C:CH$ , by the action of sulphuric acid; by boiling ortho-amido-phenyl-propionic acid with water (*Ber.*, 15, 2153); and in slight quantity on heating acetanilide,  $C_6H_5.NH.CO.CH_3$ , with  $ZnCl_2$  (*Ber.*, 16, 73). It is a thick, yellow oil, which boils at  $242-352^{\circ}$ , and possesses a characteristic sweetish, lasting odor. A pine splinter dipped into the aqueous solution of its hydrochloride is colored an intense orange-red. It is very stable, and cannot form an inner condensation product. Acetic anhydride converts it into the acetate,  $C_6H_4(NH.C_2H_3O_2).CO.CH_3$ , which yields bromides, affording *indigo* when shaken with sodium hydroxide and air. (*Ber.*, 17, 963.)

**m-Amido-acetophenone** results on reducing meta-nitro-acetophenone. It consists of yellow crystals, melting at  $93^{\circ}$ . **Para-Amido-acetophenone** is obtained by reducing the para-nitro body, and also on boiling aniline with acetic anhydride and  $ZnCl_2$  (*Ber.*, 17, 1613). It crystallizes in flat needles, and melts at  $106^{\circ}$ .

**Oxyacetophenones.**

These are produced when di- and tri-valent phenols are heated with glacial acetic acid and  $ZnCl_2$  to  $156^{\circ}$  (*Journ. pr. Chem.*, 23, 147, 546).

**Resacetophenone**,  $C_6H_3(OH)_2.CO.CH_3$ , from resorcinol, melts at  $142^{\circ}$ , and may be obtained by fusing  $\beta$ -methyl umbelliferon with potassium hydroxide.

**Quinacetophenone**,  $C_6H_3(OH)_2.CO.CH_3$ , from hydroquinone, melts at  $202^{\circ}$ .

**Gallacetophenone**,  $C_6H_2(OH)_3.CO.CH_3$ , from pyrogallie acid, melts at  $168^{\circ}$ .

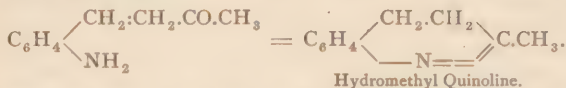
**Phenyl-ethyl Ketone**,  $C_6H_5.CO.C_2H_5$ , propiophenone, results when a mixture of calcium benzoate and propionate is distilled, or when zinc ethyl acts upon benzoyl chloride,  $C_6H_5.COCl$ . It boils at  $208-210^{\circ}$ . Nascent hydrogen converts it into secondary propyl alcohol (p. 509); chromic acid breaks it up into benzoic and acetic acids.

**Phenyl-propyl Ketone**,  $C_6H_5.CO.C_3H_7$ , obtained from calcium benzoate and butyrate, boils at  $220-222^\circ$ . Chromic acid decomposes it into benzoic and propionic acids. The isomeric **Phenylisopropyl Ketone**,  $C_6H_5.CO.C_3H_7$ , from calcium benzoate and butyrate, boils at  $215^\circ$ , and is converted into benzoic, acetic and carbonic acids by chromic acid.

**Benzyl-methyl Ketone**,  $C_6H_5.CH_2.CO.CH_3$ , Phenyl acetone, results in the distillation of calcium alphaltolate and acetate, and when zinc methyl acts on alphaltolic chloride,  $C_6H_5.CH_2.COCl$ . It boils at  $214-216^\circ$ , unites with primary sodium sulphite, and decomposes with chromic acid into benzoic and acetic acids. When its nitro-product is treated with zinc dust and ammonia, an amido-derivative of the ortho-series is first formed— $C_6H_4(NH_2).CH_2.CO.CH_3$ , but this loses water and becomes methyl ketol:—



**Phenyl ethyl methyl Ketone**,  $C_6H_5.CH_2.CH_2.CO.CH_3$ , Benzyl acetone, is formed from calcium cinnamate and acetate, and from benzyl aceto-acetic ester (p. 222). It boils at  $235^\circ$ , and when the nitro-product is reduced condensation ensues in the ortho-amido-derivative first produced, with formation of hydromethyl quinoline,  $C_{10}H_{13}N$ :—



**Benzyl-ethyl Ketone**,  $C_6H_5.CH_2.CO.C_2H_5$ , results from  $\alpha$ -toluic chloride by the action of zinc ethyl. It boils at  $226^\circ$ , and is oxidized by chromic acid to benzoic and propionic acids.

*Diketones* (p. 200).

**Benzoyl Acetone**,  $C_6H_5.CO.CH_2.CO.CH_3$  (p. 522), melts at  $58^\circ$ , distils without decomposition, and readily volatilizes with steam. It has a penetrating odor. It dissolves in caustic alkalies, and is again separated by  $CO_2$ . Ferric chloride colors it an intense red. **Ortho-Nitrobenzoyl Acetone**,  $C_6H_4(NO_2).CO.CH_2.CO.CH_3$ , melts at  $55^\circ$ . It combines with two molecules of phenyl hydrazine, and benzoyl acetone with but one; the latter likewise reacts with but one molecule of hydroxylamine (*Ber.*, 17, 814).

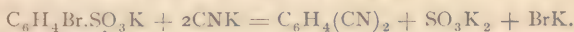
**Acetophenone-acetone**,  $C_6H_5.CO.CH_2.CH_2.CO.CH_3$ , is obtained from acetophenone chloride and aceto-acetic ester (p. 522). It is a yellow oil, insoluble in alkalies, not volatile with aqueous vapor, and does not combine with sodium bisulphite. It can combine with but one molecule of phenyl hydrazine or hydroxylamine (*Ber.*, 17, 913).

See further *Dibenzoyl methane*,  $(C_6H_5.CO)_2CH_2$ , and *tribenzoyl methane*,  $(C_6H_5.CO)_3CH$ .

## NITRILES.

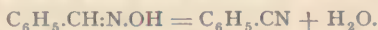
The nitriles of the benzene series, the compounds of the benzene nucleus with the cyanogen group, are formed, like the fatty nitriles, by distilling the alkali benzene sulphonates with potassium cyanide or yellow prussiate of potash (p. 475), and by the action of  $P_2O_5$  or  $PCl_5$  upon the ammonium salts and amides of the aromatic acids (p. 242). "

When the halogen benzene-sulphonic acids are distilled with CNK the halogen atoms are also replaced by cyanogen groups and we get dicyanides :—



The direct replacement of the halogens in the benzene hydrocarbons is of exceptional occurrence, *e. g.*, when chlor- and brom-benzene are conducted over strongly ignited potassium ferrocyanide, or when benzene iodide is heated to  $300^\circ$  with silver cyanide, the product being cyan-benzene.

Further, the nitriles of both the benzene and the paraffin series are formed when acetyl chloride or anhydride acts on the *aldoxims* (*Ber.*, 17, 1571):—



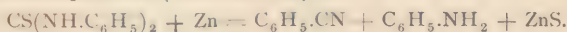
The methods of formation peculiar to the benzonitriles are :—

1. To heat the phenyl mustard oils with copper free of cuprous oxide or with zinc dust :—

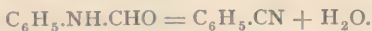


The mustard oils can be easily obtained from the anilines, and in this manner there occurs a successive conversion of the anilines into nitriles and acids (p. 445).

When the diphenylthiureas (p. 447) are heated with zinc dust, both nitriles and anilines are produced (*Ber.*, 15, 2508):—

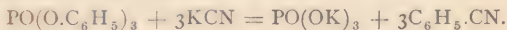


2. The distillation of the formanilines (p. 441) with concentrated hydrochloric acid or with zinc dust (*Ber.*, 17, 73):—



Both reactions generally afford but a small outcome.

3. The distillation of the triphenyl phosphates (p. 482) with potassium cyanide or ferrocyanide (*Ber.*, 16, 1771):—



4. The transformation of the isomeric nitriles or carbylamines (p. 445) through the agency of strong heat :—



The benzonitriles are similar to those of the fatty acids, and like them, when acted upon by alkalies or acids, afford the corresponding aromatic acids. With alcohols and HCl, with hydroxylamine and with anilines, they combine to HCl-imido-ethers, oximido-ethers and benzenyl amidines (p. 527).

**Benzonitrile**,  $\text{C}_6\text{H}_5.\text{CN}$ , Cyanbenzene, is isomeric with phenyl carbylamine,  $\text{C}_6\text{H}_5.\text{NC}$  (p. 445), and is best obtained from benzene sulphonic acid. It is an oil with an odor resembling that of oil of bitter-almonds, and boils at  $191^\circ$ ; its specific gravity = 1.023 at  $0^\circ$ . Like all nitriles it unites with the halogens, the halogen hydrides, and hydrogen. Acids and alkalies saponify it to benzoic acid.

Substituted benzonitriles have been obtained from the substituted benzamines.



*Meta-nitrobenzonitrile*,  $C_6H_4(NO_2).CN$ , is almost the sole product in the nitration of benzonitrile. It consists of needles, melting at  $117^\circ$ .

On dissolving benzonitrile in fuming sulphuric acid it becomes isomeric **Cyanphenine**,  $(C_6H_5.CN)_3$  (see Cyanmethine, p. 243), which melts at  $231^\circ$ . It also results when benzenylamidine (p. 527) is heated. Nascent hydrogen changes it (in presence of ammonia) into lophine (p. 514).

**Cyantoluene**,  $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown CN \end{smallmatrix}$ , Tolunitrile. The three isomerides result from the three corresponding toluidines by their conversion into mustard oils, and then heating with copper (see above). The ortho- and para-bodies are also obtained from the toluene sulphonic acids. The *ortho* boils at  $204^\circ$ : the *meta* has not yet been prepared in pure form; the *para* crystallizes in needles, melts at  $28.5^\circ$ , and boils at  $218^\circ$ . They change to the corresponding toluic acids when saponified.

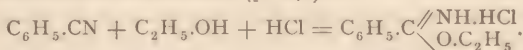
**Benzyl cyanide**,  $C_6H_5.CH_2.CN$ , is isomeric with the cyan-toluenes. This is the chief ingredient of several cresses, and is artificially prepared from benzyl chloride,  $C_6H_5.CH_2Cl$ , with potassium cyanide. It boils at  $229^\circ$ , and yields alphaltoluic acid by saponification.

The nitration of benzyl cyanide chiefly affords para-**Nitrobenzyl cyanide**,  $C_6H_4(NO_2).CH_2.CN$ , and slight quantities of the ortho- and meta-bodies (*Ber.*, 17, 505); the latter can also be made from ortho- and meta-nitrobenzalcohol by means of the chloride (*Ber.*, 16, 2064). The saponification of the three nitrobenzyl cyanides produces the nitrophenyl-acetic acids. The **Amidobenzyl cyanides**,  $C_6H_4(NH_2).CH_2.CN$ , result from the reduction of the nitrobenzyl cyanides with tin and hydrochloric acid. When diazotized, the para- and meta-compounds yield **oxybenzyl cyanides**,  $C_6H_4(OH).CH_2.CN$ , which further form oxyphenyl acetic acids,  $C_6H_4(OH).CH_2.CO_2H$  (*Ber.*, 17, 506).

**Dicyanbenzenes**,  $C_6H_4(CN)_2$ , result from the three brombenzene sulphonic acids, and on distilling the benzene-disulphonic acids with potassium cyanide. The *meta*-body (also obtained from isophthalamide) melts at  $156^\circ$ ; the *para*- at  $220^\circ$ ; the former yields isophthalic and the latter terephthalic acid.

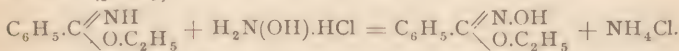
In this connection may be mentioned the *imido-ethers* and *oximido-ethers*, also the *benzenylamidines* and *benzenyloxamidines*.

The *imido-ethers* (their HCl-salts) result from the action of HCl upon a mixture of a benzonitrile with an alcohol (p. 248):—



**Benzimido-Ethyl Ether**,  $C_6H_5.C(NH).O.C_2H_5$ . Its hydrochloric acid salt consists of large, shining prisms, and at  $120^\circ$  decomposes into benzamide and ethyl chloride. The free ether, separated by alcoholic ammonia, is a thick oil, which decomposes when heated.

The *oximido-ethers* or *acidoxims*, result when hydroxylamine acts on the imido-ethers (p. 249):—

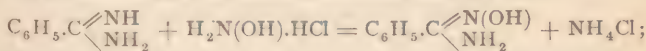


**Benzoximido-ether**,  $C_6H_5.C(N.OH).O.C_2H_5$ , is a liquid dissolving in ether, and solidifying to a crystalline mass. It is identical with the so-called **Ethylbenzo-hydroxamic Acid** (*Ber.*, 17, 1587), obtained from benzoyl chloride and hydroxylamine.

The benzenylamidines correspond perfectly to the amidines of the paraffin series (p. 249), also to the ethenyl-diphenyl-amidines, and the phenylene-amidines or anhydro-bases (p. 455).

**Benzenylamidine**,  $C_6H_5 \cdot C \begin{smallmatrix} \diagup NH \\ \diagdown NH_2 \end{smallmatrix}$ . Its HCl-salt is formed when alcoholic ammonia acts upon HCl-benzimido-butyl ether (p. 249.) The free benzenylamidine, separated by sodium hydroxide, is crystalline, melts at  $75-80^\circ$ , and at higher temperatures breaks up into  $NH_3$  and cyanphenine. **Phenylbenzenylamidine**,  $C_6H_5 \cdot C \begin{smallmatrix} \diagup NH \\ \diagdown NH \cdot C_6H_5 \end{smallmatrix}$ , results from benzonitrile or thiobenzamide,  $C_6H_5 \cdot CS \cdot NH_2$ , when heated with aniline hydrochloride (p. 249). It melts at  $112^\circ$ , and when distilled affords benzonitrile and aniline. Symmetrical **Diphenyl-benzenylamidine**,  $C_6H_5 \cdot C(N \cdot C_6H_5) \cdot NH \cdot C_6H_5$ , obtained from benzenyl anilide,  $C_6H_5 \cdot CO \cdot NH \cdot C_6H_5$ , or benzotrichloride,  $C_6H_5 \cdot CCl_3$ , by means of aniline hydrochloride, melts at  $144^\circ$ . Unsymmetrical  $C_6H_5 \cdot C(NH) \cdot N(C_6H_5)_2$ , from benzonitrile and diphenylamine, melts at  $111^\circ$  (*Ann.*, 192, 4).

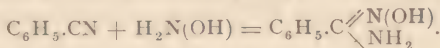
The *Oxamidines* or *Amidoxims* are produced: 1, by the action of hydroxylamine hydrochloride upon the benzenylamidines (*Ber.*, 17, 185):—



2, by the same reagent upon the imido-ethers, when probably ammonium chloride acts on the oximido-ethers first formed (*Ber.*, 17, 1588 and 1694):—



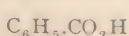
3, from the nitriles by direct union with hydroxylamine (*Ber.*, 17, 1685):—



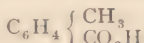
**Benzenylamidoxim**,  $C_6H_5 \cdot C \begin{smallmatrix} \diagup N(OH) \\ \diagdown NH_2 \end{smallmatrix}$ , crystallizes from ether in large plates, and melts at  $79-80^\circ$ . It affords the isonitrile reaction with chloroform and potassium hydroxide. Nitrous acid changes it to benzamide,  $C_6H_5 \cdot CO \cdot NH_2$ . With acids and caustic alkalis it yields salts, e. g.,  $C_6H_5 \cdot C(N \cdot OH) \cdot NH_2 \cdot HCl$  and  $C_6H_5 \cdot C(NH_2) : N \cdot OK$ . Alkyl iodides convert the latter into oximido-ethers, e. g.,  $C_6H_5 \cdot C(NH_2) : N(O \cdot C_2H_5)$ , which nitrous acid changes to ethers of *benzhydroxamic acid*,  $C_6H_5 \cdot C \begin{smallmatrix} \diagup N(OR) \\ \diagdown OH \end{smallmatrix}$ , probably identical with the *hydroxamic ethers* (*Ber.*, 17, 1690). Sodium amalgam converts benzenyl amidoxims into benzaldehyde and benzaldoxim.

## ACIDS.

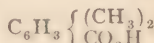
The so-called aromatic acids are derived by replacing hydrogen in the benzenes by carboxyls:—



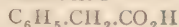
Benzoic Acid



Toluic Acids

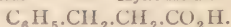


Xylic Acids.

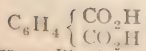


Alphatoluic Acid or

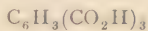
Phenylacetic Acid



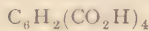
Hydrocinnamic or

 $\beta$ -Phenylpropionic Acid.

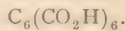
Benzene Dicarboxylic Acids



Benzene Tricarboxylic Acids



Benzene Tetracarboxylic Acids



Mellitic Acid.

The important general methods of forming the aromatic acids are:—

1. The oxidation of the hydrocarbons with a chromic acid mixture, potassium permanganate or dilute nitric acid. The side-chains are directly converted, by chromic acid, into  $\text{CO}_2\text{H}$ ; the hydrocarbons,  $\text{C}_6\text{H}_5\cdot\text{CH}_3$ ,  $\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_7$ , etc., all yield benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$ . With nitric acid it is sometimes possible to merely oxidize only the most extreme carbon atom of the side-chain. Should several side-chains chance to be present, chromic acid will almost invariably oxidize them all directly to  $\text{CO}_2\text{H}$ . Thus, the xylenes,  $\text{C}_6\text{H}_4(\text{CH}_3)_2$ , yield dicarboxylic acids,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ . Dilute nitric acid forms mono-carboxylic acids, *e. g.*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_3 \\ \diagdown \\ \text{CO}_2\text{H} \end{smallmatrix}$ , and  $\text{MnO}_4\text{K}$  produces both varieties.

Only the *para*- and *meta*-derivatives (the former more readily than the latter) of benzenes, carrying two side-chains (the xylenes and toluic acids), are oxidized to acids by chromic acid, while the *ortho*- are either not attacked at all or completely destroyed. Nitric acid, or better, potassium permanganate, oxidizes all (even the *ortho*-derivatives) to their corresponding acids. The haloid toluenes (p. 424), the nitro-toluenes (p. 429), and toluene sulphonic acids (p. 478) deport themselves similarly. The same is observed with dialkyl benzenes, where the entrance of a negative group hinders the oxidation of the alkyl occupying the *ortho*-place (*Ber.*, 15, 1022).

In the homologous phenols the  $\text{OH}$ -group completely prevents the oxidation of the alkyls by the oxidizing agents mentioned; this is true, too, in all the isomerides; but it does occur in a peculiar manner, if the phenyl hydrogen be replaced by allylic groups or acid radicals (p. 494).

In the derivatives with two different alkyls (*e. g.*, cymene,  $\text{C}_6\text{H}_4(\text{CH}_3)(\text{C}_3\text{H}_7)$ ), the higher alkyl is usually attacked first, by nitric acid or chromic acid, and converted into carboxyl (*Ber.*, 11, 619); while in the animal organism the methyl group suffers oxidation.  $\text{MnO}_4\text{K}$  occasions at first an entrance of  $\text{OH}$  in the propyl group, accompanied often by a transposition (p. 270, and *Ber.*, 14, 1135).

Consult *Ber.*, 16, 53, and 2296, upon the oxidation with ferricyanide of potassium.

In oxidizing the benzenes with chromic acid it is customary to employ a mixture of  $\text{Cr}_2\text{O}_7\cdot\text{K}_2$  (2 parts) with sulphuric acid (3 parts), which is diluted with 2–3 volumes of  $\text{H}_2\text{O}$ , and apply it in the quantity necessary for oxidation ( $\text{Cr}_2\text{O}_7\cdot\text{K}_2$  yields 3O and oxidizes 1 $\text{CH}_3$ ). The mixing is performed in a flask, provided with a long, upright tube, the whole boiled for some time, until all the chromic acid is reduced and the solution has acquired a pure green color. The product is diluted with water, the solid acid filtered off and purified by dissolving in soda, etc. Soluble acids are extracted with ether; the volatile ones distilled over with steam.

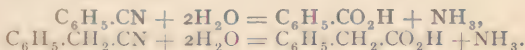
When oxidizing with nitric acid, take acid diluted with 3 parts water and boil for some time, in connection with a return condenser (2–3 days). To remove the nitro-acids, which are invariably formed, the crude product is digested with tin and concentrated hydrochloric acid; this converts the nitro- into amido-acids, which dissolve in hydrochloric acid.

Potassium permanganate often effects the oxidation at ordinary temperatures.

The substance or (with acids) its alkaline solution, is shaken with an excess of permanganate; manganese dioxide separates, while the potassium salt of the acid produced passes into the solution.

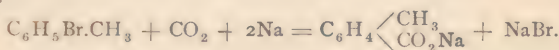
2. Oxidation of the aromatic aldehydes and alcohols.

3. The conversion of the nitriles (p. 524) when boiled with alkalis or acids (p. 168).

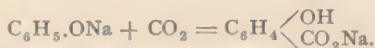


Hydrochloric acid changes the oxychlorides (obtained from the aldehydes and ketones with  $\text{CNH}$ , p. 151), to oxy-acids (p. 271). Sometimes in this case chlorinated acids first form, and are converted into oxy-acids by boiling with alkalis (see Mandelic acid).

4. Action of sodium and  $\text{CO}_2$  upon mono-brombenzenes—*Kekulé* :—

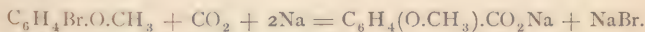


The phenols react directly with  $\text{CO}_2$  and sodium, forming oxy-acids—*Kolbe* :—

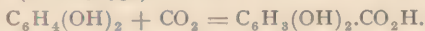


Instead of letting sodium and carbon dioxide act on the free phenols, it is better to expose the alkaline phenates to heat, in a current of  $\text{CO}_2$ -gas (see Salicylic Acid). If the  $\text{CO}_2$  should act further above  $300^\circ$ , oxyisophthalic acid and oxytrimesic acid will result.

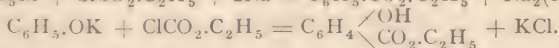
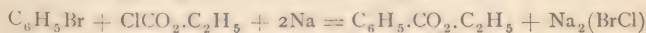
In the substituted phenols (their ethers) the halogen atom is replaced by the carboxyl-group :—



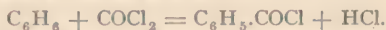
The dioxypheols of the meta-series (resorcinol, orcinol) can be changed to dioxyacids when heated with ammonium carbonate or potassium dicarbonate and water to  $110^\circ$  (*Ber.* 13, 930) :—



5. A similar reaction is the action of sodium and esters of chlorcarbonic acid upon phenols and brom-hydrocarbons—*Würtz* :—

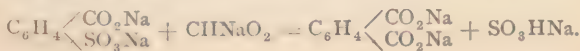


6. The action of phosgene gas upon benzene in the presence of  $\text{AlCl}_3$  (p. 412); at first acid chlorides are produced, and these change further into benzene-ketones :—



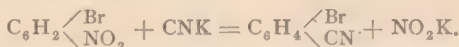
Similarly, phosgene and esters of chloroxalic acid act directly upon dimethyl aniline (p. 438).

7. Fusion of salts of sulphonic acids of the hydrocarbons, or of the aromatic acids with sodium formate :—





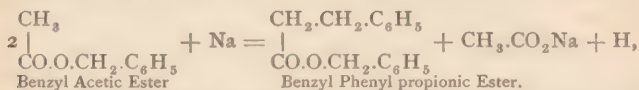
8. By heating the halogen nitro-derivatives of the hydrocarbons with CNK and alcohol, to 200–230°, in sealed tubes:—



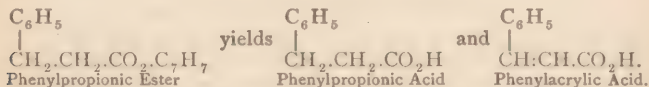
The nitrile immediately becomes an acid. In this reaction the cyanogen-group displaces  $\text{NO}_2$ , but does not assume the same position in the benzene nucleus (*Ber.*, 8, 1418).

9. Action of benzyl chlorides upon ethers of sodium acetoacetic ester, and the decomposition of the first-formed ketonic esters with alkalis (p. 218). Benzyl malonic acid,  $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ , is similarly formed from sodium malonic ester; it loses  $\text{CO}_2$  and becomes benzyl propionic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (p. 169).

10. Action of sodium upon the benzyl esters of the fatty acids; here, too, esters are produced at first:—

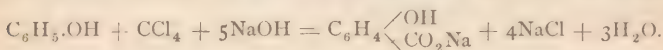


but subsequently they afford saturated and unsaturated acids (*Ann.*, 193, 321 and 204, 200):—



Phenyl butyric and phenyl crotonic acids are obtained, in the same manner, from benzyl propionic esters.

11. A very common and convenient method of producing *oxy-acids* consists in acting upon phenols, substituted phenols and also oxy-acids, with  $\text{CCl}_4$  and alkaline hydroxides (*Ber.*, 10, 2185):—

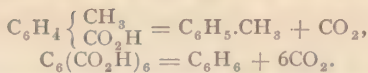


This reaction is perfectly analogous to that of chloroform upon the phenols (p. 518); only para-derivatives, however, are obtained.

The aromatic acids occur naturally, partly in a free state, partly as compounds in many resins and balsams, and in the animal organism (hippuric acid, tyrosin). They arise also in the decay of albuminoid bodies (*Ber.*, 16, 2313).

The aromatic acids are crystalline solids, which generally sublime undecomposed. They are mostly difficultly soluble in water, hence are precipitated from their salt solutions by mineral acids. Sodium amalgam or zinc dust will reduce some to aldehydes, and heating with concentrated hydriodic acid or phosphonium iodide

to hydrocarbons. When heated with lime or soda-lime, they afford hydrocarbons, with elimination of the carboxyl groups:—



From the polycarboxylic acids we obtain, as intermediate products, acids having fewer carboxyl groups, *e. g.*, phthalic acid first yields benzoic acid and then benzene:—



The hydrogen of the benzene nucleus in the acids can sustain substitutions like those observed with the hydrocarbons and phenols. In other respects they are very similar to the fatty acids, and afford corresponding derivatives.

### MONOBASIC ACIDS.

**Benzoic Acid**,  $\text{C}_7\text{H}_6\text{O}_2 = \text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$ , occurs free in some resins, chiefly in gum benzoïn (from *Styrax benzoin*); as hippuric acid in the urine of herbivorous animals. In addition to the general synthetic methods it is obtained from benzotrichloride,  $\text{C}_6\text{H}_5 \cdot \text{CCl}_3$ , when heated with water to  $150^\circ$ , or by mixing with sulphuric acid; also by boiling benzyl chloride,  $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{Cl}$ , with some dilute nitric acid, or by acting on benzene with  $\text{CO}_2$  in the presence of aluminium chloride.

*Preparation.*—Gum benzoïn is sublimed in an iron pan, covered with a paper cone. Or the powdered resin is boiled with milk of lime, some lime water (to decolorize the dye stuffs) added to the filtered solution of the lime salt, and the benzoic acid precipitated with hydrochloric acid. A more advantageous method is the production of the acid from hippuric acid (benzoyl glycol, p. 533). To accomplish this, boil the latter for an hour with 4 parts concentrated hydrochloric acid, and filter off the separated benzoic acid. Benzoic acid results from phthalic acid by heating the calcium salt to  $300\text{--}350^\circ$  (see above) with 1 molecule of calcium hydroxide.

Benzoic acid crystallizes in white, shining needles or leaflets, melts at  $120^\circ$ , and distils at  $250^\circ$ . It volatilizes readily, and is carried over with steam. It is difficultly soluble in cold water (1 part in 600 parts), but dissolves readily when heated. The vapors possess a peculiar odor, which produces coughing.

The acid yields benzene and  $\text{CO}_2$  when heated with lime; with excess of the latter benzophenone also results. Sodium amalgam converts it into benzaldehyde, hydrobenzoïn and hydrobenzoic acid,  $\text{C}_7\text{H}_{10}\text{O}_2$ .

The benzoates are mostly quite readily soluble in water. Ferric chloride throws out a reddish precipitate of ferric benzoate from their neutral solutions.

The *potassium salt*,  $2\text{C}_7\text{H}_5\text{KO}_2 + \text{H}_2\text{O}$ , crystallizes in concentrically grouped

needles. The *calcium salt*,  $(C_7H_5O_2)_2Ca + 3H_2O$ , consists of shining prisms or needles. The *silver salt*,  $C_7H_5AgO_2$ , crystallizes from hot water in bright leaflets.

The *esters* of benzoic acid, as well as those of all other aromatic acids, are prepared by conducting  $HCl$  into an alcoholic solution of the acid, and are aromatic-smelling liquids. The *methyl ester*,  $C_7H_5O_2.CH_3$ , boils at  $199^\circ$ , the *ethyl ester* at  $213^\circ$ , the *amyl ester* at  $261^\circ$ . The *isopropyl ester* boils about  $218^\circ$  and decomposes into benzoic acid and propylene. The *benzylic ester*,  $C_6H_5.CO.O.C_7H_7$ , occurs in the Peru- and Tolu-balsam,\* and is formed when benzoyl chloride acts upon benzal alcohol. It crystallizes in needles, melts at  $20^\circ$ , and boils above  $345^\circ$ . The *phenyl ester*,  $C_6H_5.CO.O.C_6H_5$ , is formed from benzoyl chloride and phenol, or by fusing benzoic acid with phenol and  $POCl_3$  (p. 481); it melts at  $66^\circ$ .

**Benzoyl Chloride**,  $C_6H_5.COCl$ , results when benzoic acid is distilled with  $PCl_5$ , and when chlorine acts upon benzaldehyde. It is an oil with a penetrating odor; boils at  $199^\circ$ , and is slowly converted into benzoic acid with water. Excess of  $PCl_5$  converts it into benzotrichloride,  $C_6H_5.CCl_3$ . *Benzoyl bromide*, from benzoic acid with  $PBr_3$ , boils at  $217^\circ$ – $220^\circ$ .

Hydroxylamine converts benzoyl chloride (or cyanide) into so-called *Benzhydroxamic acid*,  $C_6H_5.C(N.OH).OH$ , melting at  $125^\circ$ ; its ethers are the benzoximido-ethers. *Dibenzhydroxamic acid*,  $(C_6H_5CO)_2N(OH)$ , results at the same time. It melts at  $153^\circ$ .

**Benzoyl Cyanide**,  $C_6H_5.CO.CN$ , is formed when benzoyl chloride is distilled with potassium or mercury cyanide. It crystallizes in large tables which melt at  $34^\circ$  and boil at  $208^\circ$ . When boiled with alkalis it becomes benzoic acid and  $CNK$ ; concentrated hydrochloric acid affords benzoyl-formic acid.

**Benzoic Anhydride**,  $(C_7H_5O)_2O$ , is obtained by heating dry sodium benzoate (6 parts) to  $130^\circ$  with  $PCl_3O$  (1 part), or upon digesting acetyl chloride with lead nitrate (*Ber.*, 17, 1282). It consists of prisms insoluble in water, melts at  $42^\circ$ , and boils at  $360^\circ$ . It changes to the acid on boiling with water.

**Benzoyl Peroxide**,  $(C_7H_5O)_2O_2$ , forms large crystals, melts at  $100^\circ$  and deflagrates.

**Thiobenzoic Acid**,  $C_6H_5.CO.SH$ , results when benzoyl chloride acts upon alcoholic potassium sulphide. It is crystalline, melts at  $24^\circ$  and distils in aqueous vapor. Its ethyl ester boils at  $243^\circ$ . When its ethereal solution is exposed to the air the acid soon becomes *Benzoyl disulphide*  $(C_7H_5O)_2S_2$ , brilliant crystals, which melt at  $128^\circ$ . *Benzoyl sulphide*  $(C_7H_5O)_2S$ , is obtained when benzoyl chloride acts upon thiobenzoic acid. It crystallizes from ether in large prisms, melts at  $48^\circ$  and decomposes when distilled.

**Dithiobenzoic Acid**,  $C_6H_5.CS.SH$ , is obtained when  $C_6H_5.CCl_3$  is boiled with alcoholic potassium sulphide;  $C_7H_5Cl_3 + 2K_2S = C_7H_5S_2K + 3KCl$ . The free acid is very unstable. The lead salt crystallizes from carbon disulphide in red needles.

**Benzamide**,  $C_6H_5.CO.NH_2$ , results when benzyl chloride or benzoic ester acts upon alcoholic ammonia. It is best obtained by heating benzoic acid and ammonium thiocyanate to  $170^\circ$ . It crystallizes in pearly leaflets, melts at  $128^\circ$ , and boils near  $288^\circ$ . It is readily soluble in hot water, alcohol and ether.

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\* *Peru- and Tolu-balsams* are thick, yellow-brown liquids, which are obtained from the bark of varieties of *myroxylon*. In addition to resins and some free benzoic and cinnamic acids; they contain also benzyl-benzoic and cinnamic esters (*Cinnameïn*).

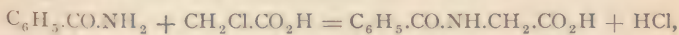
It combines with HCl to  $C_7H_7ON.HCl$ ; when it is boiled with mercuric oxide we obtain the crystalline compound  $C_6H_5.CO.NH_2$ .

**Methylene-dibenzamide**,  $CH_2(NH.CO.C_6H_5)_2$ , is identical with the so-called *hipparaffin* obtained in the oxidation of hippuric acid with  $PbO_2$  and nitric acid, and results from benzonitrile and methene dimethylate. It melts at  $223^\circ$  and when heated with water is decomposed into benzamide and formaldehyde.

**Dibenzamide**,  $(C_7H_5O)_2NH$ , results from the action of sulphuric acid upon benzonitrile. It melts at  $148^\circ$  and dissolves in sodium hydroxide to the salt  $(C_7H_5O)_2N.Na$ .

On mixing aniline and benzoyl chloride we get **Phenyl-benzamide**,  $C_7H_5O.NH.C_6H_5$ , benzoyl anilide, melting at  $158^\circ$ .

**Hippuric Acid**,  $C_9H_9NO_3 = CH_2 \begin{smallmatrix} \text{NH} \cdot C_7H_5O \\ \text{CO}_2H \end{smallmatrix}$ , **Benzoyl glycocoll**, occurs in considerable amount in the urine of herbivorous animals, sometimes in that of man. Benzoic acid, cinnamic acid, toluene and other aromatic substances, when taken internally, are eliminated as hippuric acid. It can be obtained artificially by heating benzamide with monochloroacetic acid:—



or by the action of benzoyl chloride on silver glycocollide (*Ber.*, 15, 2741), or by heating benzoic anhydride with glycocoll (*Ber.*, 17, 1662).

To prepare it, boil the urine of horses with milk of lime, filter, concentrate the solution, and precipitate with hydrochloric acid. To purify the crude acid digest it with chlorine water, or dissolve it in dilute sodium hydroxide, add sodium hypochlorite, boil to decolorization, and then precipitate the cold solution with hydrochloric acid.

Hippuric acid crystallizes in rhombic prisms, and dissolves in 600 parts cold, and readily in hot water and alcohol. It melts at  $187^\circ$ , and about  $240^\circ$  decomposes into benzoic acid, benzonitrile and prussic acid.

Its *silver salt*,  $C_9H_8AgNO_3$ , crystallizes from water in silky needles. The *ethyl ester* is best obtained by digesting glycocoll ester with benzoic anhydride; it is crystalline, melts at  $60^\circ$ , and decomposes when distilled.

Boiling acids or alkalis decompose hippuric acid into benzoic acid and glycocoll. Nitrous acid converts it into **benzoyl glycollic acid**,  $CH_2 \begin{smallmatrix} \text{O} \cdot C_7H_5O \\ \text{CO}_2H \end{smallmatrix}$ , which crystallizes in fine needles. It is easily soluble in hot water, is monobasic, and yields salts which are readily soluble.

Potassium chlorate and hydrochloric acid produce chlorinated hippuric acids. Meta-nitrohippuric acid,  $C_9H_8(NO_2)NO_3$ , is obtained by adding hippuric acid to a mixture of nitric and sulphuric acid. It affords shining prisms, which are not very soluble in water, and melt about  $150^\circ$ . When boiled with acids it breaks up into glycocoll and *meta-nitrobenzoic acid* (p. 535).

### Substituted Benzoic Acids.

These are formed by the direct substitution of benzoic acid or by oxidizing substituted toluenes. The action of the halogens (or



of hydrochloric acid and potassium chlorate; of bleaching lime and of antimony chloride) upon benzoic acid is not as ready as upon the hydrocarbons; the mono-substitution products of the *meta* series (p. 428) are almost the sole products. In the action of nitric acid small quantities of ortho- and para- compounds also result. The mono-substituted toluenes of the *meta* and *para* series are readily oxidized by chromic acid to the corresponding substituted benzoic acids, whereas the ortho-derivatives are attacked with difficulty and then completely decomposed (p. 501). However, the ortho-compounds are oxidized to the corresponding benzoic acids by dilute nitric acid, or by an excess of potassium permanganate. Thus (1, 2)-brom-, iodo- and nitro-toluene yield (1, 2)-brom-, iodo- and nitrobenzoic acids. Furthermore, substituted benzoic acids can be obtained from the oxy-acids by  $\text{PCl}_5$  and also from the amido-benzoic acids (by forming the diazo-compound and boiling with the haloid acids). When the halogen nitrobenzenes are heated with CNK substituted benzoic acids are the products. The ortho- melt at the lowest temperatures, are rather readily soluble in water, and yield easily soluble barium salts, whereby they can usually be quite readily separated from the meta- and para-derivatives. When they are fused with KOH oxy-acids result.

**Monochlorbenzoic Acids**,  $\text{C}_6\text{H}_4\text{Cl.CO}_2\text{H}$ . The *ortho* body was formerly called chlorsalicylic acid, and may be obtained from salicylic acid,  $\text{C}_6\text{H}_4(\text{OH}).\text{CO}_2\text{H}$ , by the action of  $\text{PCl}_5$ ; the chloride formed at first  $\text{C}_6\text{H}_4\text{Cl.CO.Cl}$ , (boiling at  $240^\circ$ ) is decomposed by boiling water. It sublimes in needles, melting at  $137^\circ$  (they melt below  $100^\circ$  in water). They can also be obtained from (1, 3)-chlornitrobenzene by the action of CNK. *Metachlorbenzoic Acid* (1, 3) is produced by oxidizing (1, 3)-chlortoluene, and from benzoic acid by boiling it with hydrochloric acid and  $\text{ClO}_3\text{K}$ , with  $\text{HCl}$  and  $\text{MnO}_2$ , with bleaching lime or with  $\text{SbCl}_5$ ; also from chlorhippuric acid, and from (1, 4)-chlornitrobenzene with CNK. It sublimes in flat needles, melting at  $153^\circ$ . *Parachlorbenzoic Acid* (1, 4), called chlondracrylic acid, is obtained from (1, 4)-chlortoluene; it sublimes in scales, and melts at  $240^\circ$ .

**Monobrombenzoic Acids**,  $\text{C}_6\text{H}_4\text{Br.CO}_2\text{H}$ . The *ortho*-acid, from ortho-bromtoluene (with nitric acid) and from orthoamidobenzoic acid (on heating the perbromide of the diazo-compound with alcohol), sublimes in needles, and melts at  $147\text{--}148^\circ$ ; its barium salt is very soluble in water. The *common metabrombenzoic acid*, obtained from (1, 3)-bromtoluene, and by heating benzoic acid and bromine to  $120\text{--}130^\circ$  (with some 1, 2-brombenzoic acid), sublimes in needles, melting at  $155^\circ$ . (1, 4)-*Brombenzoic Acid*, from parabromtoluene, is almost insoluble in water, crystallizes in needles, and melts at  $251^\circ$ .

**Moniodo-benzoic Acids**,  $\text{C}_6\text{H}_4\text{I.CO}_2\text{H}$ . The *ortho*-acid from ortho-iodo toluene (by means of nitric acid) and ortho-amidobenzoic (by decomposition of the diazo-compound with hydriodic acid) forms needles and melts at  $159^\circ$ . It affords salicylic acid on fusion with KOH. *Metaiodobenzoic Acid* (1, 3), from meta-iodo-toluene and meta amidobenzoic acid, sublimes in needles, and melts at  $187^\circ$ ; it affords (1, 3) oxybenzoic acid when fused with KOH. *Paraiodo-benzoic Acid* (1, 4), from paraiodo-toluene, paraiodo-propyl benzene and para-amidobenzoic acid, crystallizes from alcohol in pearly leaflets, sublimes in scales and melts at  $257^\circ$ . When fused with KOH it yields paraoxybenzoic acid.

**Fluorbenzoic Acids**,  $C_6H_4Fl.CO_2H$ . These are obtained by boiling the three diazoamido-benzoic acids with hydrofluoric acid. The *ortho*-acid melts at  $118^\circ$ , the *meta*-acid at  $124^\circ$ , and the *para*-acid at  $181^\circ$  (*Ber.*, 15, 1197). They separate out in urine as fluorhippuric acids.

**Nitrobenzoic Acids**,  $C_6H_4(NO_2).CO_2H$ .

Metanitrobenzoic acid is the principal product in the nitration of benzoic acid. The quantity of the *ortho* (20 per cent.) and *para* (1.8 per cent.) acids is less.

*Preparation*.—Gradually add sulphuric acid (4 parts) to a mixture of fused and pulverized benzoic acid (1 part) with nitre (2 parts) and apply heat to the mass until it melts, then pour the fused acids off from the potassium sulphate. To effect their separation convert them into barium salts and recrystallize; the barium salt of the *meta*-acid is very difficultly soluble (*Ann.*, 193, 202). In the nitration of cinnamic acid *para*- and *ortho*-nitro-cinnamic acids are formed. The oxidation of these yields the corresponding nitrobenzoic acids. The nitration of hippuric acid affords a nitrohippuric acid, which yields metanitrobenzoic acid. The nitrobenzoic acids can also be prepared by oxidizing the three nitrotoluenes (p. 429), and *ortho*- and *para*-nitrobenzyl chloride (p. 424) with  $KMnO_4$ .

(1, 2)-*Nitrobenzoic Acid* crystallizes in needles or prisms, melts at  $147^\circ$ , possesses a sweet taste and dissolves in 164 parts  $H_2O$  at  $16^\circ$ . The ordinary (1, 3)-*nitrobenzoic acid* crystallizes in needles or leaflets, sublimes in white needles and melts at  $142^\circ$ . After slow cooling it melts at  $135$ – $136^\circ$  and dissolves in 465 parts water at  $16.5^\circ$ . (1, 4)-*Nitrobenzoic acid*, also obtained by oxidizing *para*-nitrotoluene, forms yellowish leaflets, melts at  $240^\circ$  and dissolves with difficulty in water.

When the (1, 3)-brombenzoic acids are nitrated they yield two nitrobrombenzoic acids, the one melting at  $251^\circ$ , the other, much more soluble in water, at  $141^\circ$ . In both the nitro-group is contained in the *ortho*-position and hence in reduction both yield (1, 2)–(1, 6)-amidobenzoic acid (p. 408).

**Dinitrobenzoic Acid**,  $C_6H_3(NO_2)_2.CO_2H$ . (1, 2, 4— $C(O)_2H$  in 1) is formed by oxidizing  $\alpha$ -dinitro-toluene with fuming nitric acid, and consists of long prisms, melting at  $169^\circ$ . In the reduction with tin and hydrochloric acid the carboxyl group is split off and (1, 3)-diamidobenzene results.

The nitration of (1, 3)-nitrobenzoic acid with nitric and sulphuric acid affords the *symmetrical dinitrobenzoic acid* (1, 3, 5), which is also obtained by oxidizing symmetrical dinitrotoluene. It crystallizes from water in large quadratic plates, melting at  $205^\circ$ . Its reduction affords a diamidobenzoic acid which yields (1, 3)-diamidobenzene, when distilled with baryta.

The nitration of (1, 2)-nitrobenzoic acid produces three *dinitrobenzoic acids*: (1, 2, 6) (1, 2, 5) and (1, 2, 4)—the latter being identical with the acid obtained from  $\alpha$ -dinitrotoluene. The first acid melts at  $202^\circ$  and when heated decomposes into  $CO_2$  and (1, 3)-dinitrobenzene. The second melts at  $177^\circ$  and when reduced yields a diamidobenzoic acid which affords (1, 3)-diamido-benzene when distilled with baryta (see the diamido-benzoic acids).

**Amido-benzoic Acids**,  $C_6H_4(NH_2).CO_2H$ .

These are obtained by reducing the corresponding nitrobenzoic acids with tin and hydrochloric acid, or with hydrogen sulphide in ammoniacal solution. In the latter case the amido-acid is precipi-

tated from the solution by acetic acid. They are also formed by the oxidation of the acetyl toluidines (p. 452). Dimethylated amido-acids are produced by the action of  $\text{COCl}_2$  upon the dimethylanilines (p. 529): or by methylating the acids by heating with alkyl iodides and caustic alkali. Like glycocoll, the amido-benzoic acids yield crystalline salts both with acids and bases.

**Ortho-amidobenzoic Acid** (1, 2) also results from the two nitro-metabrombenzoic acids (p. 535) by reduction and by the action of sodium amalgam. It was first obtained from *indigo*, hence termed *anthranilic acid*.

It is prepared by oxidizing indigo with boiling  $\text{MnO}_2$  and sodium hydroxide, or more readily if orthonitrobenzoic acid be reduced with tin and hydrochloric acid. Also by the oxidation of aceto-ortho-toluidine with  $\text{MnO}_4\text{K}$  and boiling with hydrochloric acid.

The formation of dibromanthranilic acid, when bromine acts upon boiling orthonitrotoluene (p. 429) is worthy of note.

Anthranilic acid sublimes in long needles, is readily soluble in hot water and alcohol, melts at  $144^\circ$ , and decomposes into  $\text{CO}_2$  and aniline when rapidly heated. Nitrous acid converts it, in aqueous solution, into salicylic acid.

The inner anhydride (lactam) of ortho-amidobenzoic acid is the so-called **Anthranil**,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{NH} \end{smallmatrix}$ , obtained by the reduction of ortho-nitrobenzaldehyde with tin and glacial acetic acid (*Ber.*, 15, 2105, 16, 2227); it also results when ortho-nitro-phenyloxyacrylic acid is boiled with water (*Ber.*, 16, 2222). It is an oil which volatilizes readily with aqueous vapor, possesses a peculiar odor and boils with decomposition about  $210^\circ$ . It dissolves in alkalies, forming salts of anthranilic acid; by reduction ortho-amidobenzaldehyde and benzalcohol are produced. Chlorcarbonic esters produce **Anthranilcarbonic Acid**,  $\text{C}_6\text{H}_4 \begin{pmatrix} \text{CO} \\ \text{N} \end{pmatrix} \text{CO}_2\text{H}$ , which melts at  $230^\circ$  and decomposes into  $\text{CO}_2$  and anthranil.

**Acetyl-anthranilic Acid**,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{NH.CO.CH}_3 \end{smallmatrix}$ , results when acetyl-ortho-toluidine is oxidized, when ortho-amidobenzoic acid and anthranil (see above) are acted on with acetic anhydride, and in the oxidation of methyl ketol and quinaldine (see these). It forms flat needles, melts at  $180^\circ$  and is readily decomposed into acetic and anthranilic acid. **Benzoyl-anthranilic Acid** melts at  $182^\circ$ .

**o-Benzam-oxalic Acid**,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{NH.CO.CO}_2\text{H} \end{smallmatrix}$ , Oxalyl-amido-benzoic acid, carbostyric acid, kynuric acid, is prepared synthetically by heating anthranilic acid with oxalic acid to  $130^\circ$  (*Ber.*, 17, 401 and *Ref.*, 110); it is also obtained from indoxyllic acid, from carbostyryl, aceto-tetra-hydroquinoline, kynurene and kynurenic acid (see these). It crystallizes from hot water in long needles containing 1 molecule of  $\text{H}_2\text{O}(\text{C}_6\text{H}_7\text{NO}_5.\text{H}_2\text{O})$ , and melts with decomposition at  $200^\circ$ . In a dessicator, more rapidly at  $70-80^\circ$ , it loses water and evolves  $\text{CO}_2$  at  $100^\circ$ . When digested with alkalies it is decomposed into anthranilic and oxalic acids. Its *ethyl ester*, from the ester of indoxanthinic acid (*Ber.*, 15, 778), melts at  $180^\circ$ .

Similar compounds, *e. g.*, benzamoxalic acid, are prepared, too, from meta-amidobenzoic acid, by means of oxalic and malonic acids (*Ber.*, 17, 402).

**Meta-amidobenzoic Acid** (1, 3), from meta-nitrobenzoic acid, consists of aggregations of needles, dissolves readily in hot water and melts at 173–174°. It reacts acid, forming salts with acids and bases. The ethyl ester, obtained by reducing m-nitrobenzoic ester, is a thick oil. When in aqueous solution nitrous acid converts it into ordinary oxy-benzoic acid. Cyanogen chloride acts on it to form meta-cyanamido-benzoic acid,  $C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown NH.CN \end{smallmatrix}$ . This yields uramido-ben-

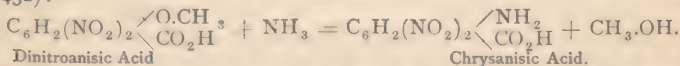
zoic acid,  $C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown NH.CO.NH_2 \end{smallmatrix}$ , with hydrochloric acid (p. 308). The latter is produced also by fusing together meta-amido-benzoic acid and urea, or by mixing the hydrochloric acid salt with potassium cyanate. It contains 1 molecule of  $H_2O$ , and forms small needles. When heated it becomes urea-dibenzoic acid,  $CO(NH.C_6H_4.CO_2H)_2$  (*Ber.*, 15, 2122).

**Para-amidobenzoic Acid**, from para-nitrobenzoic acid, or from para-toluidine, crystallizes in needles, is rather easily soluble in water, and melts at 186–187°. Nitrous acid converts it into para-oxybenzoic acid.

The amido-benzoic acids, just like the anilines (p. 471), are changed, through the diazo-compounds, into **Hydrazinebenzoic Acids**,  $C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown NH.NH_2 \end{smallmatrix}$ . Of these the ortho-body (from anthranilic acid), is the one which, when exposed to a

temperature of 230°, forms the *inner anhydride*,  $C_6H_4 \begin{smallmatrix} \diagup CO- \\ \diagdown NH.NH \end{smallmatrix}$  (*Ber.*, 14, 478).

**Dinitro-para-amidobenzoic Acid**,  $C_6H_2(NO_2)_2 \begin{smallmatrix} \diagup NH_2 \\ \diagdown CO_2H \end{smallmatrix}$ , **Chrysanic Acid**, results when dinitro-anisic and dinitro-ethyl-para-oxybenzoic acids are digested with aqueous ammonia. The group  $O.CH_3$  is supplanted by  $NH_2$  (p. 432):—



Dinitroanisic Acid

Chrysanic Acid.

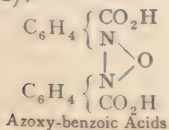
Chrysanic acid forms light, golden-yellow leaflets or needles, melts at 259° and sublimes.

**Diamidobenzoic Acids**,  $C_6H_3(NH_2)_2.CO_2H$ . Four of the six possible isomerides are known. The elimination of  $CO_2$  by one of them affords para-phenylene diamine, two others give ortho-, and the third meta-phenylene diamine. These acids conduct themselves towards the diazo-benzene-sulphonic acids, just the same as the corresponding phenylene-diamines (*Ber.*, 15, 2197).

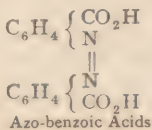
**Triamido-benzoic Acid**,  $C_6H_2(NH_2)_3.CO_2H$  (1, 3, 4, 5— $CO_2$  in 1), has been obtained from dinitro-para-amidobenzoic acid. It yields (1, 2, 3)-triamido-benzene upon distillation (p. 454). For the isomeric acid (1, 3, 5, 6) see *Ber.*, 15, 2200.

## AZO-BENZOIC ACIDS.

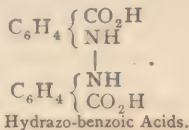
The action of sodium amalgam upon the mononitro-benzoic acids produces (same as from the nitrobenzenes) azoxy-, azo- and hydrazo-benzoic acids (p. 462):—



Azoxy-benzoic Acids



Azo-benzoic Acids



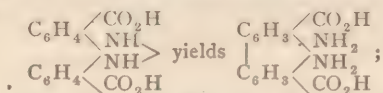
Hydrazo-benzoic Acids.



**Meta-azobenzoic Acid**,  $C_{14}H_{10}N_2O_4 + \frac{1}{2}H_2O$ , is precipitated by hydrochloric acid as a yellow, amorphous powder, and only dissolves with difficulty in water, alcohol and ether. When distilled it sustains decomposition. It is a dibasic acid, and yields crystalline yellow salts and ethers. Azobenzene is formed by the distillation of the copper salt; the calcium salt yields azo-diphenylene,  $C_{12}H_8N_2$ . Para-azo-benzoic acid is a red, amorphous powder.

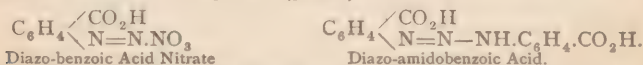
**Azoxy-benzoic Acid**,  $C_{14}H_{10}N_2O_5$  (1, 3), is formed when the alcoholic solution of meta-nitrobenzoic acid is boiled with potassium hydroxide. Hydrochloric acid precipitates it in yellowish masses.

**Hydrazo-benzoic Acid**,  $C_{14}H_{12}N_2O_4$  (1, 3), is obtained when ferrous sulphate is added to the boiling sodium hydroxide solution of azobenzoic acid. Hydrochloric acid precipitates the acid in yellow flakes from the filtered solution. It is difficultly soluble in hot alcohol. The aqueous solution of its salts absorbs oxygen, and changes to azobenzoic acid. When boiled with hydrochloric acid it is converted into the isomeric diamido-diphenyl-dicarboxylic acid, derived from diphenyl:—

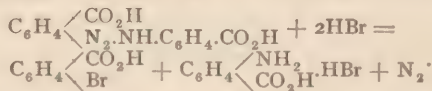


this resembles the formation of benzidine from hydrazo benzene (p. 468). The latter acid is converted, by distillation with baryta, into benzidine and  $CO_2$ .

**Diazo-compounds.** The aromatic amido-acids, analogous to the anilines, form diazo- and diazo-amido-compounds (p. 456):—



The diazo-compounds are produced by the action of nitrous acid upon salts of the amido-acids in aqueous or alcoholic solution, and sustain transpositions perfectly similar to those of other diazo-compounds. The addition of nitrous acid to the alcoholic solution of the free amido-acids causes the separation of the difficultly soluble diazo-amido acids. These are produced, too, on mixing solutions of the nitrates of the diazo-acids with amido-acids. When boiled with haloid acids they decompose into substituted acids and amido-acids, which continue dissolved as salts:—



**m-Diazo-benzoic Acid Nitrate**,  $C_7H_5N_2O_2.NO_3$ , from (1, 3)-amidobenzoic acid, is soluble with difficulty in cold water, and separates in colorless prisms which explode violently. Caustic potash precipitates a yellow and very unstable mass from the aqueous solution. This is probably the free acid. Boiling with water changes it to oxybenzoic acid. Bromine precipitates the *perbromide*,  $C_7H_5N_2O_2Br_3$ , as an oil from the aqueous solutions; it solidifies in yellow prisms. It affords meta-brombenzoic acid when digested with alcohol. Aqueous ammonia converts the perbromide into the *diazomide*,  $C_7H_5N_2O_2N$  (p. 461), which crystallizes from alcohol and ether in white leaflets. It is an acid, and forms salts with bases.

**Diazo-meta-amidobenzoic Acid**,  $C_{14}H_{11}N_3O_4$ , is precipitated as an orange-red crystalline powder when nitrous acid is led into the alcoholic solution of meta-amidobenzoic acid. It is almost insoluble in water, alcohol and ether. It is a

feeble, dibasic acid; the salts are very unstable in aqueous solution. When heated with the haloid acids it yields the corresponding halogen benzoic acids (see above).

Ortho and para-amido-benzoic acids yield corresponding diazo- and diazo-amido-compounds.

*Sulpho-benzoic Acids*,  $C_6H_4 \begin{smallmatrix} \diagup SO_2OH \\ \diagdown CO_2H \end{smallmatrix}$ .

On heating benzoic acid for some time with fuming sulphuric acid, or by conducting the vapors of  $SO_3$  into the acid, we obtain as chief product *Metasulphobenzoic Acid*, and in smaller amount *Parasulphobenzoic Acid*. The latter is readily produced by oxidizing paratoluene sulphonic acid (p. 478) with chromic acid. Both yield easily soluble needles; the first is deliquescent. The barium salt of the para-acid is the more difficultly soluble in water. When the acids are fused with potassium hydroxide meta- and para-oxy-benzoic acids result; isophthalic and terephthalic acids are the products when fused with sodium formate.

$\alpha$ -Disulphobenzoic Acid,  $C_6H_3 \begin{smallmatrix} \diagup CO_2H \\ \diagdown (SO_3H)_2 \end{smallmatrix}$  (1, 3, 5), has been obtained by heating benzoic acid with fuming sulphuric acid and  $P_2O_5$ . When distilled with CNK, meta-dicyanbenzene (p. 526) is formed, and this yields isophthalic acid. An isomeric acid ( $\beta$ ) is produced by oxidizing toluene disulphonic acid.

## HOMOLOGUES OF BENZOIC ACID.

*Acids*,  $C_8H_8O_2$ .

1. Toluic Acids,  $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown CO_2H \end{smallmatrix}$ , Methyl-benzoic Acids.

**Orthotoluic Acid** (1, 2) results from orthoxylene when oxidized with dilute nitric acid (p. 528), from orthocyantoluene (p. 526), from ortho-iodo-toluene on heating with chlorcarbonic esters and sodium, and from ortho-toluidine after its conversion into the mustard oil (p. 525). It passes over very readily with aqueous vapor, dissolves rather easily in hot water, and crystallizes from the latter in long needles, melting at  $102.5^\circ$ . The *calcium salt*,  $(C_8H_7O_2)_2Ca + 2H_2O$ , and the *barium salt*,  $(C_8H_7O_2)_2Ba + 2H_2O$ , are readily soluble in water, and crystallize in delicate needles. Chromic acid decomposes it, yielding  $CO_2$ ; potassium permanganate forms phthalic acid. For the nitro-ortho-toluic acids, see *Ber.*, 17, 162.

**Metatoluic Acid** (1, 3) is obtained by boiling crude xylene with dilute nitric acid (p. 415) (pure metaxylene is only oxidized at  $130-150^\circ$ ); it cannot, however, be fully separated from the para-acid formed simultaneously. It is prepared pure from brom-metatoluic acid (see below) by the action of sodium amalgam, or by heating uvicic acid,  $C_6H_3(CH_3)(CO_2H)_2$ , with lime, and from meta-cyantoluene. It is more soluble in water than its two isomerides, and crystallizes in little needles, melting at  $110^\circ$ . It is easily volatilized with aqueous vapor. Chromic acid oxidizes it with ease to isophthalic acid. Its *calcium salt*,  $(C_8H_7O_2)_2Ca + 3H_2O$ , is very soluble in water, and crystallizes from alcohol in needles.

**Brom-metatoluic Acid**,  $C_8H_7BrO_2$ , is formed from the nitro-parabromtoluene melting at  $45^\circ$ , when it is heated with potassium cyanide to  $200^\circ$  and saponified with potash (p. 530).

**Paratoluic Acid** (1, 4) is obtained by boiling paraxylene or cymene for several days with dilute nitric acid. The crude acid is treated at once with tin and hydrochloric acid (p. 528), to free it of adhering nitro-acids. It is also obtained from parabromtoluene, according to the method of Kekulé or of Würtz

(p. 529); and from paracyantoluene (obtained from paratoluidine and paratoluene sulphonic acid). It crystallizes from alcohol or hot water in needles, melting at  $180^{\circ}$ , and subliming readily; it boils at  $275^{\circ}$  (corrected). Its *calcium salt*,  $(C_8H_7O_2)_2Ca + 3H_2O$ , consists of readily soluble needles. Nitric acid or chromic acid oxidizes it to terephthalic acid.

**2. Phenyl-acetic Acid,  $C_6H_5 \cdot CH_2 \cdot CO_2H$ , Alphetoluic Acid,** is obtained: from benzyl cyanide,  $C_6H_5 \cdot CH_2 \cdot CN$ , when boiled with alkalis; from mandelic acid,  $C_6H_5 \cdot CH(OH) \cdot CO_2H$ , by heating with hydriodic acid; from vulpic acid by boiling with baryta; and from brombenzene and monochloracetic esters by means of sodium.

To prepare it from benzyl chloride,  $C_6H_5 \cdot CH_2Cl$ , convert the latter into cyanide, and boil this with alkalis (*Ber.*, 14, 1645), or benzaldehyde may first be changed into phenyl-chloracetic acid,  $C_6H_5 \cdot CHCl \cdot CO_2H$  (see mandelic acid) and the latter then reduced by zinc dust in ammoniacal solution (*Ber.*, 14, 240).

Phenyl-acetic acid crystallizes in shining leaflets, resembling those of benzoic acid; it melts at  $76.5^{\circ}$ , and boils at  $262^{\circ}$ . Benzoic acid is formed when it is oxidized with chromic acid.

If the acid be acted upon by chlorine or bromine in the cold the halogens will enter the benzene nucleus and in the para-position; if heat be applied the side-chain will be substituted. The latter mono-halogen derivatives are also produced from mandelic acid,  $C_6H_5 \cdot CH(OH) \cdot CO_2H$ , if it be heated with hydrochloric or hydrobromic acid to  $130$ – $140^{\circ}$ , and when boiled with alkalis regenerate mandelic acid. **Phenyl-chloracetic Acid**,  $C_6H_5 \cdot CHCl \cdot CO_2H$ , is also directly prepared from CNH benzaldehyde (see Mandelic Acid), crystallizes in leaflets, and melts at  $78^{\circ}$ . **Phenyl bromacetic Acid** melts at  $83$ – $84^{\circ}$ , and when CNK acts upon its ester diphenyl-succinic acid is produced.

**Phenyl-isonitroso-acetic Acid**,  $C_6H_5 \cdot C(N.OH) \cdot CO_2H$ , is produced from phenyl-glyoxylic acid (p. 546) with hydroxylamine, and melts at  $128^{\circ}$  (*Ber.*, 16, 1620). The *ethyl ester*, melting at  $113^{\circ}$ , has been obtained from nitrophenyl-isonitroso-acetic ester (*Ber.*, 16, 519).

**Phenyl-amido-acetic Acid**,  $C_6H_5 \cdot CH(NH_2) \cdot CO_2H$ , results from phenyl-isonitroso-acetic acid by reduction with tin and hydrochloric acid; from phenyl-bromacetic acid with ammonia, and from CNH-benzaldehyde,  $C_6H_5 \cdot CH(OH) \cdot CN$ , by ammonia and saponification. It consists of pearly leaflets, melting at  $256^{\circ}$ .

*Nitrophenyl-acetic Acids*,  $C_6H_4(NO_2) \cdot CH_2 \cdot CO_2H$ .

The para-nitro-acid, with a small amount of the ortho-nitro-acid, is produced on dissolving phenyl-acetic acid in cold, fuming nitric acid. These can be separated by means of their barium salts. The three nitro-acids may be obtained synthetically from the three nitrobenzyl cyanides,  $C_6H_4(NO_2) \cdot CN$  (p. 526).

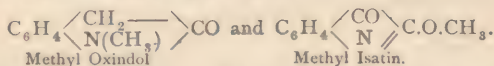
**o-Nitrophenyl-acetic Acid** crystallizes from hot water in needles, melts at  $141^{\circ}$  ( $137^{\circ}$ ), and by oxidation yields ortho-nitrobenzoic acid. **Meta-Nitrophenyl-acetic Acid** melts at  $120^{\circ}$ . **Para-Nitrophenyl-acetic Acid** is difficultly soluble in water, and melts at  $152^{\circ}$ . Further nitration of ortho- and para-nitrophenyl-acetic acid produces **Dinitrophenyl-acetic Acid** (1, 2, 4), melting at  $160^{\circ}$ , and decomposing into  $CO_2$  and  $\alpha$ -dinitro-toluene.

*Amidophenyl-acetic Acids*,  $C_6H_4(NH_2).CH_2.CO_2H$ .

These can be obtained by reducing the nitro-acids. The ortho-compound and other ortho-amido-acids can, by the exit of water, form amid-anhydrides. This is analogous to the formation of lactones (p. 275) from oxy-acids. The oxygen may be taken from the hydroxyl or from the CO-group of carboxyl; in the first instance so-called *lactams* (inner amides) are produced, in the latter the *lactims* (inner imides):—

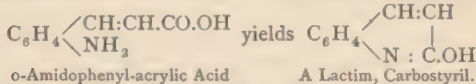
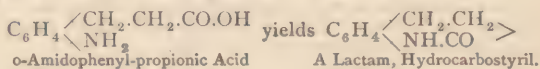


This anhydride formation sometimes occurs spontaneously in the separation of the free acids (in the reduction of the nitro-compounds). *Alkyl ethers* are produced when alkyl iodides and caustic alkalies (1 equivalent) act upon these anhydrides. With the lactams the hydrogen of the NH-group, and with the lactims that of hydroxyl, is replaced by alkyl, *e. g.* :—



The ethers of the lactams (in which the alkyl is attached to nitrogen) are very stable, whereas the lactims are decomposed by heating with hydrochloric acid.

The acids, with 2 and 3 carbon atoms in the side-chain, condense in this way; the former yield indol-, the latter quinoline-derivatives :—



The indol-bodies contain a chain of 4 C-atoms (2 of which belong to the benzene nucleus), closed by 1 N-atom (a chain of 5 members)—analogous to the pyrrol compounds (p. 399); they may also be compared to the  $\gamma$ -lactones and the furfuryl compounds. In the quinoline derivatives we have a chain of 5 C-atoms, as in the  $\beta$ -lactones. A ring of 3 C-atoms linked by N has only been confirmed in the case of anthranil (p. 536); it is, however, analogously very unstable, as in the  $\beta$ -lactones (p. 276).

The ortho-amido-derivatives of the aldehydes and ketones, in which the CO-group represents the second or third member of the side chain, are capable, too, of condensing and affording compounds belonging to the indol- and quinoline-groups. Thus, from ortho-amidophenyl-acetaldehyde we get indol (p. 518); from ortho-amidophenyl-acetone, methyl ketol (p. 524); and from ortho-amidobenzyl-acetone, hydromethyl-quinoline (p. 524). Yet, chains (with 6 and more



C-atoms and 1 N-atom) having 7 or more members, could not be produced (*Ber.*, 13, 122; 14, 481).

**o-Amidophenyl-acetic Acid** passes into its lactam, oxindol, when it is produced (by reduction of the ortho-nitro-acid). When oxindol is heated to  $150^{\circ}$  with baryta water, water is absorbed and the barium amidophenyl-acetate produced. Acids liberate oxindol from it (*Ber.*, 16, 1704).

**Acetyl-o-amido phenyl-acetic Acid**,  $C_6H_4(NH.CO.CH_3).CH_2.CO_2H$ , is obtained by dissolving acetyl oxindol in dilute sodium hydroxide; it melts at  $142^{\circ}$ , and when heated with alkalis or acids decomposes into oxindol and acetic acid.

**m-Amidophenyl Acetic Acid**, from the nitro-acid, crystallizes from hot water in leaflets, and melts at  $149^{\circ}$ . **Para-amidophenyl-acetic Acid**, from the nitro-acid, consists of pearly leaflets, and melts at  $200^{\circ}$ .

When dinitrophenyl-acetic acid (p. 540) is reduced with tin and hydrochloric acid, the **Diamido-phenyl-acetic Acid** results, and this immediately passes into para-amido-oxindol,  $C_8H_6(NH_2)NO$ . Partial reduction of the dinitro-acid with ammonium sulphide yields para-amido-ortho-nitro-phenyl-acetic acid,  $C_6H_3(NH_2)(NO_2).CH_2.CO_2H$ . This treated with amyl nitrite and alcohol affords ortho-**Nitrophenyl-isonitroso-acetic Acid**,  $C_6H_4(NO_2).C(N.OH).CO_2H$ , and ortho-nitrobenzaldoxim (p. 516). Isomeric para-**Amido-meta-nitrophenyl-acetic Acid**, from para-amidophenyl acetic acid, yields meta-nitrobenzaldoxim with the same reagents.

### *Acids, $C_9H_{10}O_2$ .*

1. **Dimethylbenzene Carboxylic Acids**,  $C_6H_3(CH_3)_2.CO_2H$ . Four of the six possible acids with this formula are known.

**Mesitylenic Acid** has the symmetrical structure (1, 3, 5), and is obtained by gradually oxidizing mesitylene with dilute nitric acid. It crystallizes from alcohol in large prisms, from water in needles; it melts at  $166^{\circ}$  and does not sublime. The *barium salt*,  $(C_9H_9O_2)_2Ba$ , is very soluble in water and consists of large, shining prisms. The *ethyl ester*,  $C_9H_9(C_2H_5)O_2$ , solidifies at  $0^{\circ}$  and boils at  $241^{\circ}$ . Distilled with excess of lime, mesitylenic acid yields isoxylene. Nitric acid oxidizes it further to uvitic and trimesic acids.

The oxidation of pseudocumene (p. 417) with dilute nitric acid produces **xylic acid**,  $C_6H_3(CH_3)_2.CO_2H$  (1, 2, 4— $CO_2H$  in 1), and so-called **para-xylic acid** (1, 3, 4); both distil with aqueous vapor and can be separated by means of their calcium salts. Xylic acid has also been obtained from bromisoxylene by the action of Na and  $CO_2$ . From alcohol it crystallizes in long prisms, is difficultly soluble in water, melts at  $126^{\circ}$  and sublimates readily. Its *calcium salt*,  $(C_9H_9O_2)_2Ca + 2H_2O$ , forms thick prisms and is more easily soluble in water than the salt of paraxylic acid. Isoxylene results when it is distilled with lime. Nitric acid oxidizes it to xylicidic acid,  $C_6H_3(CH_3).(CO_2H)_2$ ; chromic acid decomposes it to carbon dioxide.

Paraxylic acid crystallizes from alcohol in concentrically grouped needles and melts at  $163^{\circ}$ . Its *calcium salt* contains  $3\frac{1}{2}H_2O$  and consists of needles. Distilled with lime it yields ortho-xylene; both methyl groups, therefore, occur in the ortho-place. Oxidation converts it into xylicidic acid.

(2) The so-called *alpha-xylic acid*,  $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown CH_3 \end{smallmatrix}.CO_2H$  (1, 4), corresponding to alphatoluic acid, has been obtained from para-tolylecyanide,  $C_6H_4(CH_3)CH_2.CN$  (p. 509). It forms shining leaflets, melting at  $42^{\circ}$  and dissolving easily in hot water.

(3) *Ethyl-benzoic Acids*,  $C_6H_4 \begin{smallmatrix} < C_2H_5 \\ < CO_2H \end{smallmatrix}$ . The para-acid (1, 4) is obtained by oxidizing para-diethyl benzene with nitric acid, and from para-brom-ethyl benzene,  $C_6H_4Br.C_2H_5$ , by the action of Na and  $CO_2$ . It crystallizes in leaflets from hot water; melts at  $110^\circ$  and sublimes readily. Oxidation converts it into terephthalic acid. The ortho-acid is formed by reducing acetophenone carbonic acid (p. 548) with hydriodic acid. It melts at  $62^\circ$ .

(4) The *phenylpropionic acids*,  $C_6H_5.C_2H_4.CO_2H$ , are hydrocinnamic acid and hydroatropic acid:—

(1) **Hydrocinnamic Acid**,  $C_6H_5.CH_2.CH_2.CO_2H$ ,  **$\beta$ -Phenylpropionic Acid**, is obtained: by the action of sodium amalgam upon cinnamic acid (phenylacrylic acid), or upon heating the latter with hydriodic acid (*Ber.*, 13, 1680); when potassium cyanide acts upon  $\alpha$ -chloroethylbenzene,  $C_6H_5.CH_2.CH_2Cl$  (p. 416); from acetoacetic ester and malonic ester, also from benzylic acetic ester (p. 530); and in the decay of albuminoid substances. It is very easily soluble in hot water and alcohol, crystallizes in needles, melts at  $47^\circ$  and distils without decomposition at  $280^\circ$ . Chromic acid oxidizes it to benzoic acid.

*Halogen Hydrocinnamic Acids*, of the formula  $C_6H_5.CHX.CH_2.CO_2H$ , are obtained from cinnamic acid,  $C_6H_5.CH:CH.CO_2H$ , by the addition of the haloid acids (p. 179) and by the action of these upon  $\beta$ -phenyl-hydracrylic acid,  $C_6H_5.CH(OH).CH_2.CO_2H$ . On heating or boiling with water the free acids decompose (as  $\beta$ -oxyacids are produced at first, p. 273) into the haloid acid and cinnamic acid; when neutralized with alkaline carbonates they split up, even in the cold, into a halogen acid,  $CO_2$  and styrolene,  $C_6H_5.CH:CH_2$ .  **$\beta$ -Chlor-hydrocinnamic acid**,  $C_6H_5.CHCl.CH_2.CO_2H$ , melts at  $126^\circ$ ; the brom-acid at  $137^\circ$ , the iodo-acid at  $120^\circ$ .

**$\alpha\beta$ -Dibromhydrocinnamic Acid**,  $C_6H_5.CHBr.CHBr.CO_2H$ , **Cinnamic Bromide**, is formed by the addition of bromine to cinnamic acid (dissolved in  $CS_2$ ) (*Ann.*, 195, 140). It crystallizes from alcohol in leaflets, melts at  $201^\circ$ , and decomposes. When digested with a soda solution it is decomposed into  $\alpha$ -bromstyrolene,  $C_6H_5.CH:CHBr$ ,  $CO_2$  and  $HBr$ ; when boiled with water phenyl  $\alpha$ -brom-lactic acid is also produced.  **$\alpha\beta$ -Dichlorhydrocinnamic Acid** departs itself similarly, and melts at  $163^\circ$  (*Ber.*, 14, 1867).

$\alpha$ - and  $\beta$ -Monobrom-cinnamic acids are produced when dibromhydro-cinnamic acid is treated with alcoholic potassium hydroxide (see this).

#### *Phenylamido-propionic Acids.*

**Phenyl  $\alpha$ -amido-propionic Acid**,  $C_6H_5.CH_2.CH(NH_2).CO_2H$ , **Phenyl-alanine**, is produced from phenyl-acetaldehyde with  $CNH$  and ammonia (*Ann.*, 219, 186). It is soluble with difficulty in both cold water and hot alcohol. It crystallizes in leaflets or prisms. It does not part with ammonia when boiled with caustic potash or concentrated hydrochloric acid. It readily combines to form salts with bases and acids. When slowly heated it sublimes without decomposition; quickly heated we get phenyl ethylamine and a lactimide. It also occurs in the sprouts (along with asparagine) of *Lupinus luteus*, and is formed in the decay of albumen (*Ber.*, 16, 1711).

The nitration of phenyl-alanine yields the *para*-nitro-compound, which by

reduction becomes para-**Amidophenyl-alanine**,  $C_6H_4(NH_2).CH_2.CH(NH_2).CO_2H$ . The latter is obtained also in the reduction of dinitro-cinnamic acid,  $C_6H_4(NO_2).CH:C(NO_2).CO_2H$  (*Ber.*, 16, 852), and when acted upon by one equivalent of  $NO_2H$  affords tyrosine (*Ann.*, 219, 170).

**Phenyl- $\beta$ -amidopropionic Acid**,  $C_6H_5.CH(NH_2).CH_2.CO_2H$ , is obtained on treating  $\beta$ -bromhydro-cinnamic acid with aqueous ammonia; it is easily soluble in water and alcohol, melts at  $121^\circ$ , and when boiled with acids decomposes into  $NH_3$  and cinnamic acid. It does not combine with bases, and only with difficulty with acids.

The **Halogen-hydrocinnamic Acids**,  $C_6H_4.X.CH_2.CH_2.CO_2H$ , containing the substitutions in the benzene nucleus, are obtained from the corresponding halogen cinnamic acids on heating them with hydriodic acid and phosphorus (*Ber.*, 15, 2301; 16, 2040).

**Nitrohydrocinnamic Acids**,  $C_6H_4(NO_2).CH_2.CH_2.CO_2H$ .

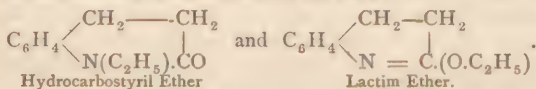
The nitration of hydrocinnamic acid produces the *para* and *ortho* acids, which can be separated by crystallization with water. **Ortho-Nitrohydrocinnamic Acid** is more easily obtained from the dinitrohydrocinnamic acid (see below). It forms small yellow crystals, and melts at  $113^\circ$ .

**m-Nitrohydrocinnamic Acid** results from para-amido-meta-nitrohydrocinnamic acid (see below) by the elimination of the amido-group, and melts at  $118^\circ$ . **p-Nitrohydro-cinnamic Acid** melts at  $163^\circ$ , and is oxidized to para-nitrobenzoic acid by a chromic acid mixture.

**Amido-hydrocinnamic Acids**,  $C_6H_4(NH_2).CH_2.CH_2.CO_2H$ .

**o-Amido-hydrocinnamic Acid**. When this acid is formed by the reduction of ortho-nitrohydrocinnamic acid with tin and hydrochloric acid it at once changes to its lactam, **Hydrocarbostyryl**,  $C_9H_9NO$  (p. 541). The latter is intimately related to quinoline,  $C_9H_7N$ , dissolves readily in alcohol and ether, crystallizes in prisms, melts at  $160^\circ$ , and distils undecomposed.

While the lactim of ortho-nitro-amido-cinnamic acid is unstable, its ethers exist, as do those of the lactam (hydrocarbostyryl) (p. 541):—



The former is produced from hydrocarbostyryl by means of  $C_2H_5I$  and alcoholic potassium hydroxide, and is very stable; the latter, formed in the reduction of ortho-nitrohydrocinnamic ether, is saponified on heating with hydrochloric acid (*Ber.*, 15, 2103).

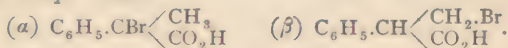
**m-Amidohydrocinnamic Acid**, prepared by reducing the meta-nitro-acid with tin and hydrochloric acid, melts at  $85^\circ$ . **p-Amido-hydrocinnamic Acid** melts at  $131^\circ$ . Strong nitration of hydrocinnamic acid produces para-ortho-dinitro-hydrocinnamic acid,  $C_6H_3(NO_2)_2.C_2H_4.CO_2H$  (1, 2, 4), which melts at  $126^\circ$ . Reduction with ammonium sulphide affords p-amido-o-nitrocinnamic acid, melting at  $139^\circ$ . By the elimination of the  $NH_2$ -group we get ortho-nitrohydrocinnamic acid. The reduction of the dinitro-acid with tin and hydrochloric acid brings about condensation of the diamido-acid at once to p-amido-hydrocarbostyryl,  $C_9H_8(NH_2).NO$  (p. 541), melting at  $211^\circ$  (*Ber.*, 15, 2291).

The p-Amido-m-nitrohydrocinnamic Acid,  $C_6H_3(NH_2)(NO_2).C_2H_4.CO_2H$ , is formed in the nitration of aceto-para-amido-hydrocinnamic acid, melts at

145°, and by the elimination of the amido-group yields meta-nitrohydrocinnamic acid.

(2) **Hydro-atropic Acid**,  $C_6H_5 \cdot CH \begin{smallmatrix} \text{CH}_3 \\ \text{CO}_2H \end{smallmatrix}$ ,  **$\alpha$ -Phenyl-propionic Acid**, is obtained from atropic acid,  $C_9H_8O_2$ , by the action of sodium amalgam. It is an oil, boiling at 265°, and is volatile in aqueous vapor. Potassium permanganate oxidizes it to atrolactic acid (p. 555) by changing tertiary hydrogen to hydroxyl.

*Bromhydro-atropic Acids* :—



Both isomerides result from the addition of HBr to atropic acid,  $C_9H_8O_2$ . The  $\alpha$ -acid, obtained from atrolactic acid,  $C_9H_{10}O_3$ , by means of hydrobromic acid, melts at 93°, and reverts to atrolactic acid on boiling with a soda solution. The  $\beta$ -acid also melts at 93°, and when boiled with alkaline carbonates yields atropic acid,  $C_9H_{10}O_3$ , together with atropic acid and styrolene. The chlorhydro-atropic acids deport themselves similarly (*Ann.*, 209, 21).

*$\alpha\beta$ -Dibromhydro-atropic Acid*,  $C_6H_5 \cdot CBr(CH_2Br) \cdot CO_2H$ , from atropic acid and bromine, melts at 115°, and when boiled with water yields acetophenone,  $C_6H_5 \cdot CO \cdot CH_3$ .

*Acids*,  $C_{10}H_{12}O_2$ .

**Durylic Acid**,  $C_6H_2(CH_3)_3 \cdot CO_2H$ , is obtained by the oxidation of durene (*Ber.*, 16, 418), crystallizes in hard prisms, and melts at 115°.

The oxidation of isodurene affords three **Isodurylic Acids**, the  $\alpha$ - melting at 215°, the  $\beta$ - at 151°, and  $\gamma$ - at 84°. When these split off  $CO_2$  the corresponding trimethyl benzenes result; from the  $\alpha$  we get hemi-mellithene, from the  $\beta$  mesitylene and from  $\gamma$  pseudocumene (*Ber.*, 15, 1855).

**Cumic Acid**,  $C_6H_4 \begin{smallmatrix} C_3H_7 \\ \text{CO}_2H \end{smallmatrix}$ , para-isopropyl benzoic acid (containing the isopropyl group), is produced by the oxidation of cuminic alcohol and aldehyde with dilute nitric acid, or by the action of potassium hydroxide (p. 507). It has been synthetically prepared from para-bromcumene,  $C_6H_4Br \cdot C_3H_7$  (with isopropyl, p. 418), by the action of sodium and  $CO_2$  (*Ber.*, 15, 1903). It is furthermore produced by the oxidation of cymene (p. 419) in the animal organism; a transposition of normal propyl occurs in this case.

It is obtained from cuminol (Roman caraway oil) by fusion with caustic potash, or what is better, by the oxidation with an alkaline potassium permanganate solution (*Ber.*, 11, 1790).

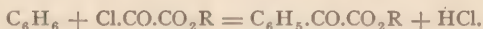
Cumic acid is very soluble in water and alcohol, crystallizes in needles or leaflets, melts at 116°, and boils about 290°. It yields cumene (isopropyl benzene) when distilled with lime. Chromic acid oxidizes it to terephthalic acid and  $MnO_4K$  to oxypropylbenzoic acid,  $C_6H_4(C_3H_6 \cdot OH) \cdot CO_2H$ , and aceto-benzoic acid (p. 548).



**Normal Cumic Acid**,  $C_6H_4(C_3H_7).CO_2H$ , para-normal propylbenzoic acid (with normal propyl), is obtained by oxidizing propylisopropyl benzene and dinormal propyl benzene with dilute nitric acid (*Ber.*, 16, 417); also synthetically from para-bromopropyl benzene,  $C_6H_4Br.C_3H_7$  (with normal propyl), by the action of  $CO_2$  and Na. It is volatile with aqueous vapor, crystallizes in shining needles or leaflets, and melts at  $140^\circ$ .

#### KETONIC ACIDS (COMPARE p. 214).

**Phenylglyoxylic Acid**,  $C_6H_5.CO.CO_2H$ , Benzoyl Formic Acid, is obtained in the action of fuming hydrochloric acid at ordinary temperatures upon benzyl cyanide,  $C_6H_5.CO.CN$  (p. 526), and by oxidizing benzoyl carbinol, styrolene alcohol (p. 509) and mandelic acid with dilute nitric acid. Its esters are formed when ethyl chloroxalic ester acts upon mercury diphenyl,  $(C_6H_5)_2Hg$ , or the amyl ester upon benzene in the presence of aluminium chloride:—



The acid is separated from its salts in the form of an oil, which slowly solidifies on standing over sulphuric acid. It is very soluble in water, melts at  $65-66^\circ$ , and when distilled decomposes into  $CO$  and benzoic acid, to a less degree into  $CO_2$  and benzaldehyde. When mixed with benzene containing thiophene and sulphuric acid, it is colored deep red, afterward blue-violet; all its derivatives, *e. g.*, isatin, react similarly.

Being a ketonic acid it (its esters) unites with sodium bisulphite. It combines with  $CNH$ , forming oxycyanides,  $C_6H_5.C(OH)(CN).CO_2H$ , from which phenyl tarttronic acid is derived. Sodium amalgam converts it into mandelic acid, and hydriodic acid and phosphorus at  $160^\circ$  into alphetoluic acid.

Hydroxylamine changes it to phenylisonitroso-acetic acid (p. 540).

**o-Nitrobenzoylformic Acid**,  $C_6H_4(NO_2).CO.CO_2H$ , is formed from ortho-nitrobenzoyl cyanide, by means of  $CNK$ , etc. It crystallizes with one molecule of water, and melts at  $47^\circ$ . When anhydrous it melts with decomposition at  $122^\circ$ . Ferrous sulphate and sodium hydroxide reduce it to

**Isatinic Acid**,  $C_6H_4(NH_2).CO.CO_2H$ , ortho-amido-phenylglyoxylic acid. It is a white powder, obtained from its lead salt by  $SH_2$ . Digestion of its solution converts it at once into its lactim—isatin,  $C_8H_5NO_2$  (p. 541).

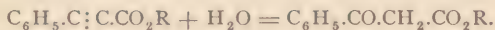
The lactam of isatinic acid,  $C_6H_4 \begin{array}{l} \diagup CO.CO \\ \diagdown NH \end{array}$  (p. 541), is unstable; the aceto-

derivative, aceto-pseudo-isatin (see this), however, is stable. It dissolves in alkalis, forming salts of **Aceto-isatinic Acid**,  $C_6H_4 \begin{array}{l} \diagup CO.CO_2H \\ \diagdown NH.CO.CH_3 \end{array}$ , from which the latter may be separated by dilute acids. The acid is difficultly soluble in cold water, crystallizes from alcohol in needles, and melts at  $160^\circ$ . Boiling hydrochloric acid decomposes it with separation of isatin. When in an acetic acid solution it is reduced to aceto-ortho-amido mandelic acid by sodium amalgam (p. 554).

**p-Dimethylamido phenylglyoxylic Acid**,  $(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$ . It is produced from dimethyl aniline and chloroxalic ester (p. 438); it melts at  $187^\circ$ .

### $\beta$ -Ketonic Acids (p. 216).

**Benzoylacetic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (isomeric with the oxyphenylacrylic acids and phenylglycidic acid), is obtained by saponifying its ester with potassium hydroxide at ordinary temperatures. It is crystalline, and melts at  $85-90^\circ$  with evolution of  $\text{CO}_2$ . Ferric chloride colors its aqueous solution a deep violet. Its *ethyl ester* arises when phenyl propiolic esters are dissolved in sulphuric acid and then diluted with water (p. 522), (*Ber.*, 16, 2128):—



It is an oil, and resembles aceto-acetic ester. It decomposes into acetophenone,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3$ ,  $\text{CO}_2$  and alcohol when boiled with water or dilute sulphuric acid. The hydrogen of its  $\text{CH}_2$ -group can be replaced by alcoholic and acid radicals.

**Benzoyl-allyl-acetic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}(\text{C}_3\text{H}_5)\cdot\text{CO}_2\text{H}$ , is isomeric with benzoyl-tetramethylene carboxylic acid (p. 395), melts at  $122-125^\circ$ , and is decomposed by alkalis into allyl-acetophenone,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot(\text{C}_3\text{H}_5)$  and  $\text{CO}_2$ .

**p-Nitrobenzoyl-acetic Acid**,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , melts at  $135^\circ$ , and is produced in a manner analogous to that of benzoyl acetic acid, *i. e.*, by heating para-nitrophenyl propiolic ester,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{K}$ , to  $35^\circ$  with sulphuric acid, while ortho-nitrophenyl propiolic ester is transposed into the isomeric isatogenic ester (*Ber.*, 17, 326).

Of the class of  $\gamma$ -ketonic acids may be mentioned

**Benzoylpropionic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which is obtained from benzene and succinic anhydride by means of  $\text{AlCl}_3$ :—



It is also formed by reducing benzoyl acrylic acid with  $\text{HgNa}$ . It melts at  $116^\circ$ , and when reduced by sodium amalgam yields a  $\gamma$ -oxy-acid, which changes to *phenylbutyrolactone* (*Ber.*, 15, 890).

The benzenes condense similarly with other dibasic acid anhydrides in the presence of  $\text{AlCl}_3$  (*Ber.*, 14, 365) (see benzoyl-acrylic acid).

### *Diketonic Acids.*

Those containing two  $\text{CO}$ -groups are variously obtained.

Benzoyl chloride converts aceto-acetic esters into those of **Benzoylaceto-acetic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{CO}\cdot\text{CH}_3 \\ \text{CO}_2\text{R} \end{smallmatrix}$  (p. 222). Their decomposition affords acetophenone and benzoyl acetone (p. 524). Thus the esters of aceto-acetic acid convert the bromide of acetophenone,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ , into esters of **Acetophenone-aceto-acetic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CO}\cdot\text{CH}_3 \\ \text{CO}_2\text{R} \end{smallmatrix}$ , and yield acetophenone acetone (p. 524).

**Dibenzoylacetic Acid**,  $(\text{C}_6\text{H}_5\cdot\text{CO})_2\text{CH}\cdot\text{CO}_2\text{H}$ . Its ester is a thick oil, and results from the action of benzoyl chloride (p. 222) upon benzoyl acetic ester. The acid crystallizes in needles, and melts at  $109^\circ$ . When boiled with water it decomposes into  $\text{CO}_2$  and **dibenzoylmethane**,  $(\text{C}_6\text{H}_5\cdot\text{CO})_2\text{CH}_2$ . The latter is a diketone, melts at  $81^\circ$ , and boils above  $200^\circ$ . It is soluble in alkalis, and is separated from the same by acids. When sodium ethylate and benzoyl chloride

act upon it **Tribenzoylmethane**,  $(C_6H_5.CO)_3CH$ , results; this melts at  $225^\circ$ , and sublimes undecomposed (*Ber.*, 16, 2135).

**Phthalylacetic Acid**,  $C_{10}H_6O_4 = C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH.CO_2H$  (?), is produced on heating phthalic anhydride with sodium acetate and acetic anhydride. It is insoluble in water, and melts under decomposition at  $245^\circ$ . It is soluble in alkalis, forming  $C_6H_4 \begin{smallmatrix} \diagup CO.CH_2.CO_2H \\ \diagdown CO_2H \end{smallmatrix}$ , so-called **benzoyl aceto-carboxylic acid**, which melts at  $90^\circ$ , and decomposes into  $CO_2$  and **acetophenone-carboxylic acid**,  $C_6H_4 \begin{smallmatrix} \diagup CO.CH_3 \\ \diagdown CO_2H \end{smallmatrix}$ , **o-aceto-benzoic acid**. The latter also results in the oxidation of oxyisopropylbenzoic acid, and melts at  $115^\circ$ . The last two acids combine with hydroxylamine (*Ber.*, 16, 1993) as ketonic acids.

Phthalic anhydride affords similar acids with propionic acid, succinic acid, etc. (*Ber.*, 14, 919).

**Quinisatinic Acid**,  $C_6H_4 \begin{smallmatrix} \diagup CO.CO.CO_2H \\ \diagdown NH_2 \end{smallmatrix}$ , ortho-amido-phenyl mesoxalylic acid. It is obtained by oxidizing  $\beta\gamma$ -dioxycarbostyryl with ferric chloride. From water it crystallizes in yellow prisms. Heated to  $120^\circ$  it becomes a lactim—quinisatin,  $C_6H_4 \begin{smallmatrix} \diagup CO.CO \\ \diagdown N \end{smallmatrix} = C.OH$ . This is analogous to the formation of isatin from isatinic acid (*Ber.*, 16, 2219, and 17, 985).

## MONOBASIC OXY-ACIDS.

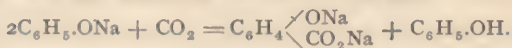
The aromatic oxy-acids containing hydroxyl united to the benzene nucleus, *e. g.*,  $C_6H_4.OH.CO_2H$ , combine the character of acids and phenols, hence are designated *Phenol acids*. They are obtained from the acids by fusing their halogen- or sulpho-substitution products with alkalis, or by the action of nitrous acid upon the amido-acids. They can be prepared from the homologous phenols, *e. g.*,  $C_6H_4(OH).(CH_3)$ , and the oxyaldehydes, *e. g.*,  $C_6H_4(OH).(CHO)$ , by fusion with the alkalis (p. 518). They are formed synthetically from the phenols by the action of sodium and  $CO_2$ , or upon boiling with  $CCl_4$  and an alkaline hydroxide (p. 530).

Their basicity is determined (toward carbonates) by the number of carboxyl groups present. The hydroxyl in them manifests the same deportment as in the phenols, and yields salts with strong bases, but they are again decomposed by  $CO_2$ . The ortho-oxy-acids, unlike the meta- and para-derivatives, volatilize in aqueous vapor, are colored violet by ferric chloride, and dissolve in chloroform. All the oxy-acids decompose into  $CO_2$  and phenols when distilled with lime (p. 479).

Should the hydroxyl groups enter the side-chains, we would obtain aromatic oxy-acids (alcohol acids), corresponding perfectly to the oxy-fatty acids.

**Acids**,  $C_7H_6O_3 = C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown OH \end{smallmatrix}$ , Oxybenzoic Acids.

**1. Ortho-oxybenzoic Acid,  $C_6H_4(OH).CO_2H$  (1, 2), Salicylic Acid,** occurs in a free condition in the buds of *Spiraea ulmaria*, as the methyl ester in oil of *Gaultheria procumbens* (Oil of Wintergreen) and other varieties of gaultheria, from which it may be easily obtained by saponification with potassium hydroxide. It is prepared artificially: by oxidizing saligenin and salicylic aldehyde; by action of nitrous acid upon anthranilic acid; from the two nitro-(1, 3)-brombenzoic acids (p. 535); by fusing orthochlor- and brombenzoic acids, orthotoluene sulphonic acid and ortho-cresol with alkalis; from phenol with  $CO_2$ , or with chlorcarbonic ester and sodium, or by means of  $CCl_4$  and sodium hydroxide (p. 530). Especially interesting is its production from  $CO_2$  and sodium phenoxide. This method is at present employed for its formation upon a large scale—Kolbe. When sodium phenoxide is heated in a current of carbon dioxide, the latter is absorbed, phenol distils over, and the residue is disodium salicylate:—

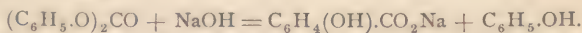


The reaction takes place even below  $100^\circ$ , but is most rapid at  $170$ – $180^\circ$ , and continues to  $300^\circ$ , when the sodium salicylate suffers decomposition. The same reaction occurs when potassium phenoxide is heated to  $150^\circ$  in a current of carbon dioxide. At a more elevated temperature, however, there is formed with the dipotassium salicylate its isomeride, dipotassium paraoxybenzoate. The latter is more abundant in proportion to the increased temperature, until at  $220^\circ$  it is the sole product. Primary potassium salicylate undergoes a similar transposition at  $220^\circ$ ; phenol then distils over and dipotassium paraoxybenzoate constitutes the residue:—



The sodium salt also decomposes in this manner, but instead of paraoxybenzoic acid it yields disodium salicylate. On the other hand, if we expose primary sodium paraoxybenzoate, at  $280$ – $290^\circ$ , in a current of  $CO_2$ , there results conversely (together with phenol) disodium salicylate. This strikingly illustrates the different deportment of potassium and sodium on fusion. The salts of the earths and heavy metals sustain no transpositions.

A similar procedure applied in the technical production of salicylic acid (by Hentschel), consists in heating phenol carbonate (p. 482) at  $200^\circ$ , with caustic soda. Phenol distils over and sodium salicylate remains:—

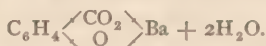


Phenol ethyl ether, etc., result in the use of sodium ethylate.

Salicylic acid consists of four-sided prisms and crystallizes readily from hot water in long needles. It dissolves in 400 parts water at  $15^\circ$ , and in 12 parts at  $100^\circ$ ; it is very soluble in chloroform. It melts at  $155$ – $156^\circ$ , and when carefully heated sublimes in needles; when quickly heated (or with water at  $220^\circ$ , more readily with



hydrochloric acid) it breaks up into  $\text{CO}_2$  and phenol. Its aqueous solution acquires a violet coloration upon the addition of ferric chloride. It is a powerful antiseptic, hence its wide application. When salicylic acid is heated with baryta water, the hydrogen atoms of both hydroxyls are replaced by barium, and there separate leaflets of the basic salt,



When boiled with lime water the basic calcium salt is precipitated as an insoluble powder. This behavior affords a means of separating salicylic from the other two oxybenzoic acids. The halogens react readily with salicylic acid, yielding substitution products. Nitration produces three nitro-salicylic acids.

$\text{PCl}_5$  converts salicylic acid into the chloride,  $\text{C}_6\text{H}_4\text{Cl.COCl}$ ,—an oil, boiling at  $240^\circ$ . Hot water converts it into orthochlorobenzoic acid (p. 273).

$\text{PCl}_3\text{O}$  produces the so-called *salicylide*,  $\text{C}_7\text{H}_4\text{O}_2 = \text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \text{O} \end{array}$  (?), which crystallizes in shining leaflets, melting at  $195^\circ$ . Boiling alkalis change it again to salicylic acid.

The *esters* of salicylic acid appear, according to the common method, by conducting  $\text{HCl}$  into the alcoholic solutions. The *methyl ester*,  $\text{C}_6\text{H}_4(\text{OH}).\text{CO}_2.\text{CH}_3$ , is the chief ingredient of wintergreen oil (from *Gaultheria procumbens*). It is an agreeably-smelling liquid, which boils at  $224^\circ$  (corrected); its sp. gr. = 1.197 at  $0^\circ$ . It dissolves in alkalis, forming unstable phenol salts. Ferric chloride gives it a violet coloration. The *ethyl ester*  $\text{C}_6\text{H}_4(\text{OH}).\text{CO}_2.\text{C}_2\text{H}_5$ , boils at  $223^\circ$ .

When the methyl ester is digested with an alcoholic solution of potassium hydroxide and methyl iodide at  $120^\circ$  (p. 480), we get the *dimethyl ester*, which is an oil boiling at  $245^\circ$ . Boiled with potassium hydroxide, it is saponified, yielding methyl alcohol and methyl salicylic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O.CH}_3 \\ \diagdown \text{CO}_2\text{H} \end{array}$ , which forms large plates, melting at  $98^\circ$ . It is soluble in hot water and alcohol. It decomposes into  $\text{CO}_2$  and anisol,  $\text{C}_6\text{H}_5.\text{O.CH}_3$ , when heated to  $200^\circ$ .

We can produce *salicylic-diethyl ester*, boiling at  $259^\circ$ , and *ethylsalicylic acid* in the same manner. The latter melts at  $19.5^\circ$ , and at  $300^\circ$  decomposes into  $\text{CO}_2$ , and ethyl phenol,  $\text{C}_6\text{H}_5.\text{O.C}_2\text{H}_5$ .

Acetyl chloride converts salicylic acid into aceto-salicylic acid,  $\text{C}_6\text{H}_4(\text{O.C}_2\text{H}_5.\text{O}).\text{CO}_2\text{H}$ , which crystallizes in delicate needles, and melts at  $218^\circ$ .

## 2. Meta-oxybenzoic Acid, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{CO}_2\text{H} \end{array}$ (1, 3), is produced:

by acting with nitrous acid upon ordinary (1, 3)-amidobenzoic acid; by fusing (1, 3)-chlor-, brom-, iodo-, and sulpho-benzoic acids and metacresol with potassium hydroxide. It also results from metacyanphenol. It usually crystallizes in wart-like masses consisting of microscopic leaflets, dissolves in 260 parts  $\text{H}_2\text{O}$  at  $0^\circ$ , and readily in hot water. It melts at  $200^\circ$ , and sublimes without decomposition. Ferric chloride does not color it. It yields  $\text{CO}_2$  and phenol when heated with alkalis.

The *ethyl ester*,  $\text{C}_6\text{H}_4(\text{OH}).\text{CO}_2.\text{C}_2\text{H}_5$ , crystallizes in plates, soluble in hot

water, and melting at 72°. It boils at 282°. The *dimethyl ester*,  $C_6H_4(O.CH_3)_2.CO_2.CH_3$ , is formed when metaoxybenzoic acid is heated with  $CH_3I$  (2 molecules) and potassium hydroxide (2 molecules) to 140°. Boiling KOH converts this into *methyl-metaoxybenzoic acid*,  $C_6H_4(O.CH_3).CO_2H$ . The latter is also obtained from the methyl ether of metabromphenol,  $C_6H_4Br.O.CH_3$ , with sodium and  $CO_2$ . It crystallizes in shining scales, is easily soluble in water, melts at 107°, and sublimes undecomposed.

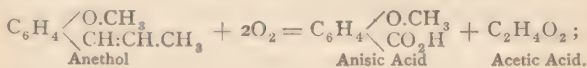
3. **Para-oxybenzoic Acid**,  $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown CO_2H \end{smallmatrix}$  (I, 4), is obtained from parachlor-, brom-, iodo-, and sulpho-benzoic acids, and also from many resins, by fusing them with potassium hydroxide. It results, too, when para-amidobenzoic acid is treated with nitrous acid or phenol with carbon tetrachloride and sodium hydroxide (together with salicylic acid). An interesting way of obtaining it consists in heating potassium phenoxide in a current of  $CO_2$  (p. 549) at  $220^\circ$ . This is the best course to pursue in preparing it (*Journal pract. Chemie*, 16, 36).

From water paraoxybenzoic acid crystallizes in monoclinic prisms, containing 1 molecule  $H_2O$ . This it loses at  $100^\circ$ . It is somewhat more easily soluble than salicylic acid (in 580 parts  $H_2O$  at  $0^\circ$ ), and melts at  $210^\circ$  with partial decomposition into  $CO_2$  and phenol. Ferric chloride does not color it, but throws down a yellow precipitate which dissolves in an excess of the reagent. Its basic *barium salt*,  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CO_2 \end{smallmatrix} Ba$ , is insoluble, and may be employed to separate the acid from its meta-isomeride.

The *methyl ester*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{CO}_2\text{CH}_3 \end{smallmatrix}$ , consists of large plates, melting at  $17^\circ$ , and distilling at  $283^\circ$ . The *ethyl ester* melts at  $113^\circ$ , and boils near  $297^\circ$ .

*Methyl-paraoxybenzoic Acid*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{CH}_3 \\ \text{CO}_2\text{H} \end{smallmatrix}$ , and *ethyl-paraoxybenzoic acid*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{C}_2\text{H}_5 \\ \text{CO}_2\text{H} \end{smallmatrix}$ , are produced the same as the corresponding compounds of the other two benzoic acids; the second melts at  $195^\circ$ .

**Anisic Acid**, called methyl paraoxybenzoic acid, is obtained by oxidizing anisol and anethol (p. 520) with nitric acid or a chromic acid mixture:—



or by oxidizing the methyl ether of para-cresol,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{O.CH}_3 \\ \diagdown \text{CH}_3 \end{smallmatrix}$ . It is prepared by oxidizing anisol with a chromic acid mixture (*Ann.*, **141**, 248).

Anisic acid crystallizes from hot water in long needles, from alcohol in rhombic prisms, melts at  $185^{\circ}$ , sublimes and boils without decomposition at  $280^{\circ}$ . Heated with baryta it breaks up into  $\text{CO}_2$  and anisol,  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_3$ . It yields paraoxybenzoic acid when heated with hydrochloric or hydriodic acid (p. 481). The salts of anisic acid are very soluble in water and crystallize well. The halogens and nitric acid afford substitution products. These yield substituted anisols by distillation with baryta.

*Acids, C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>.*

1. **Oxytoluic Acids, C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)**  $\begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$  **Cresotinic Acids.** The ten possible isomerides are known (*Ber.*, 16, 1966). They result from the toluic acids, C<sub>6</sub>H<sub>4</sub>.CH<sub>3</sub>.COOH, by the substitution of OH for one atom of hydrogen in the benzene nucleus, and from the cresols, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>).OH, by the introduction of CO<sub>2</sub>H, by means of Na and CO<sub>2</sub>, or by the carbon chloride reaction (p. 530). They can also be obtained by the oxidation (fusion with caustic alkali) of their aldehydes, C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)(OH).CHO. The latter are made from the cresols by means of the chloroform reaction. Those isomerides in which the OH occupies the ortho-place with reference to the CO<sub>2</sub>H group (4 isomerides) are, like salicylic acid, colored intensely *violet* by ferric chloride, are readily soluble in cold chloroform, and are volatile in steam. When ignited with lime the oxytoluic acids split up into CO<sub>2</sub> and the corresponding cresols, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>).OH. Some of them, especially the ortho-oxyacids, suffer this change when heated with concentrated hydrochloric acid to 200°.

2. **Oxyphenyl Acetic Acids, C<sub>6</sub>H<sub>4</sub>**  $\begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{CH}_2\text{CO}_2\text{H} \end{smallmatrix}$  **oxy-alphatoluic acids.** The para- and meta- acids can be obtained from the corresponding amidophenyl acetic acids, C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>).CH<sub>2</sub>.CO<sub>2</sub>H (p. 541), by diazotizing, and also from the oxybenzyl cyanides, C<sub>6</sub>H<sub>4</sub>(OH).CH<sub>2</sub>CN (p. 526).

*o*-Oxyphenyl Acetic Acid has been obtained from isatinic acid (and isatin), (p. 546). The diazotizing of isatin at first produces oxyphenylglyoxylic acid, C<sub>6</sub>H<sub>4</sub>(OH).CO.CO<sub>2</sub>H, which by action of sodium amalgam affords *o*-oxymandelic acid, C<sub>6</sub>H<sub>4</sub>(OH).CH(OH).CO<sub>2</sub>H. The latter on boiling with hydriodic acid yields *o*-oxy phenylacetic acid, melting at 137°. Ferric chloride colors it violet.

Being a  $\gamma$ -oxyacid it affords a lactone, C<sub>6</sub>H<sub>4</sub>  $\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{CH}_2\text{CO} \end{smallmatrix}$ , when distilled. This melts at 49°, and boils at 236° (*Ber.*, 17, 975).

*m*-Oxyphenyl Acetic Acid melts at 129°. *p*-Oxyphenyl Acetic Acid occurs in urine, and arises from the decomposition of albuminous bodies. It crystallizes in flat needles, melts at 148°, and is colored dirty-green by ferric chloride. When distilled with lime it affords CO<sub>2</sub>, and *p*-cresol C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>).OH.

3. **Oxymethylbenzoic Acids C<sub>6</sub>H<sub>4</sub>**  $\begin{smallmatrix} \diagup \text{CH}_2\text{OH} \\ \diagdown \text{CO}_2\text{H} \end{smallmatrix}$  **Mineral acids precipitate the ortho-acid** from its salts (obtained by boiling phthalid with alkalis) in the form of a powder. This melts at 118°, with decomposition into water and phthalid. It is a  $\gamma$ -oxyacid, hence by the elimination of water can yield a lactone (even by boiling with water):—



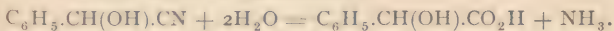
The lactone C<sub>8</sub>H<sub>6</sub>O<sub>2</sub>, called **Phthalid**, is prepared by the action of hydriodic acid, or zinc and HCl upon phthalic chloride (*Ber.*, 10, 1445). It also results from orthotolylene chloride, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Cl)<sub>2</sub>, upon boiling with water and lead nitrate. It resembles the lactones perfectly, and is but slightly soluble in cold water. It crystallizes from hot water and alcohol, in needles or plates, melts at 73°, and sublimes. It is reduced to orthotoluic acid on boiling with hydriodic acid. MnO<sub>4</sub>K oxidizes it to phthalic acid. Sodium amalgam reduces it to *hydro-*

*phthalid*, C<sub>6</sub>H<sub>4</sub>  $\begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{CH(OH)} \end{smallmatrix}$  O. The esters of benzoic acid are similarly reduced. (*Ber.*, 11, 239).

4. **Phenylglycollic Acid, Mandelic Acid, C<sub>6</sub>H<sub>5</sub>.CH(OH).**CO<sub>2</sub>H, was first obtained by heating amygdalin (p. 543) with hy-



drochloric acid, and is synthetically formed from benzaldehyde by the action of CNH and hydrochloric acid, and the transformation of the oxycyanide first produced:—



It can also be obtained from benzoylformic acid (p. 546), by reduction with sodium amalgam, and from phenylchloracetic acid (p. 540) by boiling it with alkalis.

*Preparation.*—Boil the oxycyanides either with concentrated hydrochloric acid or heat them with sulphuric acid, which has been diluted with one-half volume of water. Or the oxycyanide can be changed to phenylchloracetic acid by heating it to  $140^\circ$  with concentrated hydrochloric acid (*Ber.*, 14, 239). The oxycyanide,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CN}$ , is obtained by digesting benzaldehyde for some time with 20 per cent. prussic acid (p. 271), or by gradually adding concentrated hydrochloric acid (1 molecule), with constant stirring, to a cooled mixture of benzaldehyde with ether and pulverized CNK (1 molecule).—*Ber.*, 14, 239 and 1965. The oxycyanide is a yellow oil with an odor resembling that of prussic acid and oil of bitter almonds. It solidifies at  $-10^\circ$ , and decomposes when heated.

The natural mandelic acid, obtained from amygdalin, is optically active, and, indeed, lævo-rotatory. It forms brilliant crystals, melting at  $132.8^\circ$ . Synthetic-mandelic acid, called *paramandelic acid*, is optically inactive; it crystallizes in rhombic plates or prisms, and melts at  $118^\circ$ . It is more soluble in water than the lævo-acid (100 parts water at  $20^\circ$  dissolve 15.9 parts of the former and 8.6 parts of the latter). Both acids manifest like chemical deportment (like the tartaric acids, etc.). Dilute nitric acid converts them into benzoyl-formic acid, while by more powerful oxidation, they yield benzoic acid. When heated with hydriodic acid they form phenyl-acetic acid, with hydrobromic and hydrochloric acid chlorphenyl or bromphenyl acetic acids. Phenylglycollic acid is isomeric with mandelic acid (p. 483).

Inactive or para-mandelic acid, like racemic acid, consists of *dextro*- and *lævo*-mandelic acids (p. 42). Fermentation with *Penicillium glaucum* destroys the lævo and there remains the dextro-acid, which, so far as physical properties are concerned, resembles the so-called natural lævo-acid perfectly, only excepting the fact that the former rotates the plane equally as much to the right. Lævo-mandelic acid, however, is formed from the para-acid through the influence of a *schizomycetes* (*Vibrio*?) (*Ber.*, 17, 2723). The direct splitting-up of para-mandelic acid into the dextro- and lævo-acids can be brought about by the crystallization of the cinchonine salt. The mixing together of the dextro- and lævo-acids (molecular quantities) results in the formation of inactive paramandelic acid. When the dextro- or lævo-acid is heated in a tube to  $160^\circ$  it is converted into the inactive mandelic acid.

Of the substituted mandelic acids we know only

**o-Amido-mandelic Acid**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CH}(\text{OH})\cdot\text{CO}_2\text{H} \\ \diagdown \text{NH}_2 \end{array}$ , Hydrindic Acid. This is not stable in a free condition, but immediately passes into its lactone, dioxindol, by the splitting-off of water (p. 541). Its sodium salt is formed from isatin by the action of  $\text{NaHg}$ , and separates from the concentrated solution in brilliant crystals,  $\text{C}_8\text{H}_8\text{NaNO}_3 + \text{H}_2\text{O}$ . A more stable compound than the preceding is



**Aceto-o-amidomandelic Acid**,  $C_6H_4 \begin{smallmatrix} \diagup CH(OH).CO_2H \\ \diagdown NH.CO.CH_3 \end{smallmatrix}$ . This is obtained from aceto-isatinic acid (p. 546) by the action of NaHg, and from aceto-dioxindol by its solution in baryta water. It is very soluble in water, crystallizes in needles, and melts at  $142^\circ$ . The action of HI or NaHg causes it to break up into acetic acid and oxindol, the anhydride of ortho-amido-phenyl acetic acid (p. 542).

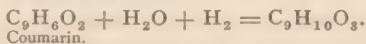
*Acids*,  $C_9H_{10}O_3$ .

1. **Oxyethylbenzoic Acid**,  $C_6H_4 \begin{smallmatrix} \diagup CH(OH).CH_3 \\ \diagdown CO_2H \end{smallmatrix}$  (ortho), is formed from acetophenone-carboxylic acid (p. 548) when treated with sodium amalgam. It yields a lactone which solidifies below  $0^\circ$  (*Ber.*, 10, 2205).

2. **Oxymesitylenic Acid**,  $C_6H_2(CH_3)_2 \begin{smallmatrix} \diagup OH \\ \diagdown CO_2H \end{smallmatrix}$  ( $CO_2H:OH = 1:2$ ), is obtained by fusing mesitylene sulphonic acid with caustic alkali, and when nitrous acid acts upon amidomesitylenic acid. It melts at  $179^\circ$ , and being an oxyacid is colored a deep blue by ferric chloride.

3. **Oxyphenylpropionic Acids**,  $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown C_2H_4.CO_2H \end{smallmatrix}$ . There are six isomerides.

**Hydro-ortho-coumaric Acid**, **Melilotic Acid**,  $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown CH_2.CH_2.CO_2H \end{smallmatrix}$  (1, 2), occurs free and in combination with coumarin in the yellow melilot (*Melilotus officinalis*), and is produced by the action of sodium amalgam upon coumaric acid and coumarin (see this):—



It crystallizes in long needles, dissolves easily in hot water, and melts at  $81^\circ$ . Ferric chloride imparts a bluish color to the solution. When distilled it passes

into the  $\delta$  lactone,  $C_9H_8O_2 = C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown C_2H_4.CO \end{smallmatrix}$ , *Hydrocoumarin*, melting at

$25^\circ$ , and boiling at  $272^\circ$ . When boiled with water it regenerates the acid. Melilotic acid decomposes when fused with alkali into salicylic acid and acetic acid; hence it is a benzene derivative of the ortho-series. *Ethyl Melilotic Acid*,  $C_6H_4(O.C_2H_5).C_2H_4.CO_2H$ , is produced by ethylating the acid and when sodium amalgam acts upon ethyl coumaric and ethyl coumarinic acids; it melts at  $80^\circ$ .

**Hydro-meta-coumaric Acid**,  $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown CH_2.CH_2.CO_2H \end{smallmatrix}$  (1, 3), is obtained from meta-coumaric acid by means of sodium amalgam; it melts at  $111^\circ$ .

**Hydro-para-coumaric Acid**,  $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown CH_2.CH_2.CO_2H \end{smallmatrix}$  (1, 4), results when NaHg acts upon para-coumaric acid, or when nitrous acid acts on para-amidohydrocinnamic acid (p. 544), and in the decay of tyrosine. It is very soluble in hot water, forms small crystals, and melts at  $125^\circ$ .

One of the derivatives of hydroparacoumaric acid is

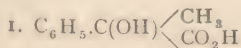
**Tyrosine**,  $C_9H_{11}NO_3 = C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown CH_2.CH(NH_2).CO_2H \end{smallmatrix}$  (1, 4),

Oxyphenyl- $\alpha$ -amidopropionic Acid, Oxyphenyl-alanine. It occurs in the liver, the spleen, the pancreas, and in stale cheese (*τὸ ρῶς*), and is formed from animal substances (albumen, horn, hair) on

boiling them with hydrochloric or sulphuric acid; by fusion with alkalis or by putrefaction (together with leucine, aspartic acid, etc.). It may be prepared synthetically from para-amido-phenyl-alanine (from phenylacetaldehyde, p. 544) by the action of 1 molecule of  $\text{NO}_2\text{K}$  upon the hydrochloric acid salt. It is soluble in 150 parts boiling water, and crystallizes in delicate, silky needles; it is very difficultly soluble in alcohol, and insoluble in ether. Mercuric oxide produces a yellow precipitate, which becomes dark red in color if it be boiled with fuming nitric acid to which considerable water has been added (delicate reaction). Being an amido-acid, tyrosine unites with acids and bases, forming salts. If it be heated to  $270^\circ$  it decomposes into  $\text{CO}_2$  and oxyphenylethyl-amine,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ . When fused with  $\text{KOH}$  it yields paraoxybenzoic acid,  $\text{NH}_3$  and acetic acid. Putrefaction causes the formation of hydroparacoumaric acid, and nitrous acid converts the tyrosine into para-oxyphenyl-lactic acid,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$  (*Ann.*, 219, 226).

**Phloreitic Acid**,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{OH} \\ \diagup \\ \text{C}_2\text{H}_4 \end{smallmatrix}\cdot\text{CO}_2\text{H}$  (1, 4), is formed together with phloroglucin when phloretine is digested with potassium hydroxide (p. 505). It crystallizes in long prisms, is very soluble in hot water, and melts at  $128\text{--}130^\circ$ . Ferric chloride colors its solution green. Baryta decomposes it into  $\text{CO}_2$  and phlorol; fusion with  $\text{KOH}$  produces paraoxybenzoic and acetic acids. The oxidation of methyl phloreitic acid yields anisic acid. Phloreitic acid, like the cresols, cannot be directly oxidized (p. 494). It is, therefore, a di-derivative of benzene and belongs to the para-series, and is probably para-oxyhydro-atropic acid,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{H}$ .

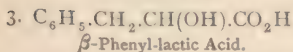
4. Phenylloxypionic Acids,  $\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$ . There are four isomerides:—



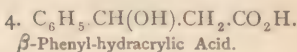
$\alpha$ -Phenyl-lactic Acid  
Atrolactic Acid



$\alpha$ -Phenyl-hydracrylic Acid.  
Tropic Acid.



$\beta$ -Phenyl-lactic Acid.



$\beta$ -Phenyl-hydracrylic Acid.

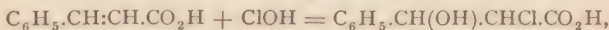
(1) The so-called **Atrolactic Acid** is obtained from  $\alpha$ -bromhydro-atropic acid (p. 545), when the latter is boiled with a soda solution, and by oxidizing hydro-atropic acid with  $\text{MnO}_4\text{K}$ . It is prepared synthetically from acetophenone,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3$ , by means of  $\text{CNH}$  and sulphuric acid or dilute hydrochloric acid, and by boiling the cyanide with concentrated hydrochloric acid we get  $\beta$ -Chlorhydro-atropic Acid (p. 545).—*Ber.*, 14, 1352 and 1980. It dissolves very readily in water, crystallizes with one-half molecule  $\text{H}_2\text{O}$  in needles or plates, and at  $80\text{--}85^\circ$  loses its water of crystallization. While yet containing water it melts at  $91^\circ$ ; when anhydrous at  $93^\circ$ . It remains unaltered when heated with baryta water, but when boiled with concentrated hydrochloric acid, it decomposes into water and atropic acid.

(2) **Tropic Acid** is obtained by digesting the alkaloids, atropine and belladonna, with baryta water. It is formed artificially, by boiling  $\beta$ -chlorhydro-atropic acid (p. 545), with a solution of potassium carbonate (*Ann.*, 209, 25). The acid is

rather more difficultly soluble in water; crystallizes in needles or plates, and melts at  $117^{\circ}$ . It decomposes into water and atropic acid when boiled with baryta water.

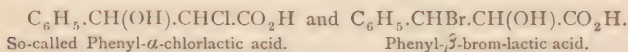
(3)  **$\beta$ -Phenyl-lactic Acid**,  $C_6H_5.CH_2.CH(OH).CO_2H$ , Benzyl-glycollic acid, is derived from phenylacetaldehyde (p. 517), with  $CNH$  and hydrochloric acid and from benzyl-tartronic acid upon heating it to  $180^{\circ}$ . The acid crystallizes from water in large prisms, melts at  $97^{\circ}$ , and when heated to  $130^{\circ}$  with dilute sulphuric acid decomposes into phenylacetaldehyde and formic acid. Boiling with water does not alter it.

(4)  **$\beta$ -Phenyl-hydracrylic Acid**,  $C_6H_5.CH(OH).CH_2.CO_2H$ , commonly called *phenyl-lactic acid*, results on boiling  $\beta$ -brom-hydro-cinnamic acid (p. 543) with water, or by the addition of hypochlorous acid to cinnamic acid:—



and then reducing the resulting chlor-acid with sodium amalgam. The acid is very soluble in cold water, and melts at  $94^{\circ}$ . When heated with dilute sulphuric acid it decomposes (like the  $\beta$ -oxy-acids) at  $100^{\circ}$  already into  $H_2O$  and cinnamic acid (together with a little styrolene) (*Ber.*, 13, 304). When digested with the haloid acids it forms phenyl- $\beta$ -halogen-propionic acids (p. 543).

Phenyl-halogen-lactic acids (p. 283).



So-called Phenyl- $\alpha$ -chlorlactic acid.

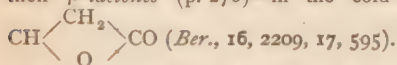
Phenyl- $\beta$ -brom-lactic acid.

The first of these is produced by the action of chlorine in alkaline solution upon phenyl-acrylic acid (cinnamic acid) (see above, and also *Ann.*, 219, 184). It crystallizes with 1 molecule  $H_2O$ , which escapes in the desiccator. When it contains water it melts at  $79^{\circ}$ , when anhydrous at  $104^{\circ}$ . **Phenyl- $\alpha$ -bromlactic Acid** is produced on boiling cinnamic dibromide (p. 543) with water. It crystallizes in leaflets, containing 1  $H_2O$ , melts at  $121^{\circ}$ , loses water of crystallization, and then melts at  $125^{\circ}$ . When boiled with alkalis both acids yield phenylacetaldehyde (p. 517), together with  $\beta$ -phenylglyceric acid (see *Ann.*, 219, 180).

**Phenyl- $\beta$ -brom-lactic Acid** (see above) is produced when hydrobromic acid acts upon  $\beta$ -phenylglyceric acid (p. 561). It has not been further described (*Ber.*, 16, 2820).

**Nitro-phenyl-lactic Acids**,  $C_6H_4(NO_2).CH(OH).CH_2.CO_2H$ .

The three isomerides (ortho, meta, and para) are obtained from the three nitro-cinnamic acids by the addition of  $HBr$ , and by the action of the alkalis, when their  $\beta$ -lactones (p. 276)—in the cold—are also produced,  $C_6H_4(NO_2)$ .



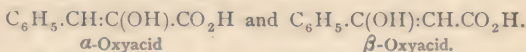
The ortho-nitro-acid results also by the condensation of ortho-nitro-benzaldehyde with acetaldehyde by means of a little baryta water, and by oxidizing the aldehyde first produced with silver oxide (*Ber.*, 16, 2206). It melts at  $126^{\circ}$ , and when heated to  $190^{\circ}$  with dilute sulphuric acid yields ortho-nitro-cinnamic acid. Its  $\beta$ -lactone melts at  $124^{\circ}$ , and decomposes on boiling with water into  $CO_2$  and ortho-nitrostyrolene; it affords hydrocarbostyryl when reduced.

The meta-nitro-acid melts at  $105^{\circ}$ ; its  $\beta$ -lactone at  $98^{\circ}$ . The para-nitro-acid melts at  $132^{\circ}$ , and its lactone at  $92^{\circ}$ . When the three nitro-acids are heated with alcoholic zinc chloride, we do not get their lactones, but their esters (*Ber.*, 17, 1659).

In concluding the phenyl-lactic acids we will mention in addition phenyl glycidic acid and the oxyacrylic acids.

**Phenylglycidic Acid**,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H}$  (p. 356), appears to be the body that results on the decomposition of benzoyl-imido-cinnamic acid (*Ber.*, 16, 2815, 17, 1616) and is also produced from phenyl- $\beta$ -bromolactic acid (together with- $\alpha$ -oxycinnamic acid, see below). It is very stable, melts at  $155^\circ$  and is colored an intense green by ferric chloride. Sodium amalgam converts it into  $\beta$ -phenyl-hydracrylic acid.

### Phenyloxyacrylic Acids, Oxycinnamic Acids,



$\alpha$ -Oxyacid

$\beta$ -Oxyacid.

Both acids are known only in their salts. When separated by acids they readily decompose with formation of phenylacetaldehyde and  $\beta$ -phenylglyceric acid (p. 561). The  $\alpha$ -oxyacid (its potassium salt) is obtained from phenyl- $\beta$ -bromolactic acid with alcoholic potash. Its ether yields  $\beta$ -phenyl-lactic acid with  $\text{HgNa}$ . The salt of the  $\beta$ -oxyacid, from phenyl- $\alpha$ -bromolactic acid (together with glycidic acid), is identical with the salt of phenyloxyacrylic acid (formerly considered phenylglycidic acid), of Glaser (*Ber.*, 16, 2823).

**o-Nitrophenyl-Oxyacrylic Acid**,  $\text{C}_6\text{H}_4(\text{NO}_2) \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{CO}_2\text{H}$  (?), from o-nitrocinnamic acid, yields indigo by fusion (*Ber.*, 13, 2262). Boiled with water it forms anthranil (p. 536) and anthroxanaldehyde.

### Acids, $\text{C}_{10}\text{H}_{12}\text{O}_3$ .

**Phenyl- $\gamma$ -oxybutyric Acid**,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is precipitated in the cold, from its salts, by hydrochloric acid. It melts at  $75^\circ$ , with decomposition into water and its lactone—**phenyl-butyrolactone**,  $\text{C}_{10}\text{H}_{10}\text{O}_2$ . The latter is obtained from phenyl-brombutyric acid (from isophenylcrotonic acid) with a soda solution. It melts at  $37^\circ$ , and boils at  $306^\circ$  (*Ann.*, 216, 103).

**Oxypropylbenzoic Acid**,  $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH})(\text{CH}_3) \cdot \text{CO}_2\text{H}$ , oxycumic acid, is obtained from cumic acid (p. 545), by the hydroxylation of the isopropyl group. This is effected by the oxidation with potassium permanganate (p. 270). It crystallizes from hot water in thin prisms, and melts at  $156^\circ$ . Its sulpho-acid is similarly formed from paracymene and paraisocymene-sulphonic acid (p. 410) with  $\text{KMnO}_4$  (*Ber.*, 14, 2391). When boiled with hydrochloric acid it parts with water, and becomes **Propenylbenzoic Acid**,  $\text{C}_6\text{H}_4 \cdot \text{C}(\text{CH}_3) : \text{CH}_2$ , which melts at  $161^\circ$ . Similarly, nitrocumic acid yields **Nitro-oxypropylbenzoic Acid** and **Nitro-propenylbenzoic Acid**, and by the reduction of the latter, the *amido acids*. Amido-oxypropylbenzoic acid yields the *cumazonic* compounds (*Ber.*, 16, 2577, 17, 1303), which are analogous in constitution to the ethenyl-amido-phenols (p. 490). With nitrous acid amido-oxypropenyl benzoic acid affords methyl-cinnolincarboxylic acid (*Ber.*, 17, 724).

## MONOBASIC DIOXYACIDS.

1. **Dioxybenzoic Acids**,  $\text{C}_7\text{H}_6\text{O}_4 = \text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO}_2\text{H}$ . These are also termed the carboxylic acids of the corresponding dioxy-benzenes,  $\text{C}_6\text{H}_4(\text{OH})_2$  (Resorcinol, pyrocatechin, hydroquinone),



since they can be obtained from the latter by the direct introduction of  $\text{CO}_2\text{H}$  (on heating with ammonium carbonate, p. 529), or by the oxidation of the corresponding aldehydes,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CHO}$  (p. 520). Three of the six possible isomerides are derived from resorcinol (1, 3), two from pyrocatechin (1, 2), and one from hydroquinone (1, 4). Conversely, by the elimination of  $\text{CO}_2$  from the acids we regenerate the dioxybenzenes.

(1) Symmetrical *Dioxybenzoic Acid* (1, 3, 5),  $\alpha$ -resorcylic acid, corresponding to orcinol, is obtained from  $\alpha$ -disulphobenzoic acid (p. 539) on fusion with  $\text{KOH}$ . It crystallizes with  $1\frac{1}{2}\text{H}_2\text{O}$ , melts at  $233^\circ$ , and by the exit of  $\text{CO}_2$  yields resorcinol. Ferric chloride does not color it. When distilled or heated with sulphuric acid to  $130^\circ$  it yields anthrachryson, a derivative of anthracene. Its *dimethyl ether*,  $\text{C}_6\text{H}_3(\text{O}\cdot\text{CH}_3)_2\cdot\text{CO}_2\text{H}$ , is produced on oxidizing dimethylorcin, and melts at  $176^\circ$ .

(2)  $\beta$ -Resorcylic Acid (1, 2, 4 —  $\text{CO}_2\text{H}$  in 1) is obtained on heating resorcinol with ammonium carbonate (p. 520), also on fusing  $\beta$ -disulphobenzoic acid (p. 539) and  $\beta$ -resorcylaldehyde (also umbelliferon) with  $\text{KOH}$ . It is difficultly soluble in cold water, crystallizes with  $1\frac{1}{2}$ ,  $2\frac{1}{2}$  (and 3) molecules  $\text{H}_2\text{O}$  in fine needles, melting in the anhydrous state at  $205^\circ$ , and decomposing into  $\text{CO}_2$  and resorcin. Ferric chloride colors it a dark red.

(3)  $\gamma$ -Resorcylic Acid (1, 2, 6 —  $\text{CO}_2\text{H}$  in 1) is formed together with  $\beta$ -resorcylic acid from resorcinol, by means of ammonium carbonate (*Ber.*, 13, 2380); it decomposes above  $150^\circ$  into  $\text{CO}_2$  and resorcinol, and is colored a blue-violet by ferric chloride. On warming it reduces alkaline copper and silver solutions.

(4) Hydroquinone Carboxylic Acid (1, 4,  $\text{CO}_2\text{H}$ ), *Oxysalicylic Acid*, was first prepared from gentisin, hence called *gentisinic acid*. It is obtained from brom-, p-iodo-, and amido-salicylic acids; also from hydroquinone by means of a potassium dicarbonate solution, and by fusing gentisinic aldehyde (from hydroquinone) with  $\text{KOH}$  (*Ber.*, 14, 1988). It melts at  $197^\circ$ , and at  $215^\circ$  breaks up into  $\text{CO}_2$  and hydroquinone. Ferric chloride colors it a deep blue. On warming it reduces alkaline copper and ammoniacal silver solutions. When oxidized it yields a yellow colored acid, which is decolorized by reducing agents, and is in all probability quinone carboxylic acid,  $\text{C}_6\text{H}_3(\text{O})_2\cdot\text{CO}_2\text{H}$ .

(5) Pyro-catechin-ortho-carboxylic Acid (1, 2, 3 —  $\text{CO}_2$  in 1) is obtained from meta-iodo-salicylic acid by fusion with  $\text{KOH}$ , and from pyrocatechin on heating with ammonium carbonate to  $140^\circ$  (together with protocatechuic acid). It crystallizes in small needles (with  $2\text{H}_2\text{O}$ ), is colored an intense blue by ferric chloride, melts at  $204^\circ$ , and decomposes further into  $\text{CO}_2$  and pyrocatechin (*Ber.*, 16, 81; *Ann.*, 220, 117).

(6) Protocatechuic Acid,  $\text{C}_6\text{H}_3\left\{\begin{array}{l} (\text{OH})_2 \\ \text{CO}_2\text{H} \end{array}\right.$  (1, 3, 4 —  $\text{CO}_2\text{H}$  in 1), Pyrocatechin-para-carboxylic acid, is obtained from many benzene tri-derivatives (*e. g.*, brom- and iodo-para-oxybenzoic acids, bromanisic acid, para- and meta-cresolsulphonic acid, eugenol, catechin), as well as from various resins (benzoïn, asafoetida, myrrh) on fusion with  $\text{KOH}$  (and usually together with some paraoxybenzoic acid); furthermore, on heating hydroquinone with ammonium carbonate (together with pyrocatechin ortho-carboxylic acid) and by the action of bromine upon quinic acid.

It is most easily prepared from kino by adding the latter to fused caustic soda (*Ann.*, 177, 188). It crystallizes with one  $H_2O$  in shining needles or leaflets, and dissolves readily in hot water, alcohol and ether. At  $100^\circ$  it loses its water of crystallization, melts at  $199^\circ$ , and decomposes further into  $CO_2$  and pyrocatechin. Ferric chloride colors the solution green; after the addition of a very dilute soda solution it becomes blue, later red (all derivatives containing the protocatechuic residue,  $(OH)_2C-$  *Ber.*, 14, 958, react similarly). Ferrous salts color its salt solutions violet. It reduces an ammoniacal silver solution, but not an alkaline copper solution.

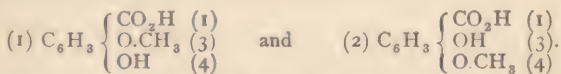
*Diprotocatechuic Acid*,  $C_{14}H_{10}O_7$ , is a tannic acid, which results on boiling the preceding with aqueous arsenic acid. It is very similar to common tannic acid, but is colored green by ferric oxide.

The dimethyl- and diethyl-protocatechuic acids are obtained by heating with potassium hydroxide and  $CH_3I$  or  $C_2H_5I$ .

*Dimethyl-protocatechuic Acid*,  $C_6H_3 \left\{ \begin{matrix} (O.CH_3)_2 \\ CO_2H \end{matrix} \right.$ , also results from dimethyl-protocatechuic aldehyde (p. 521), methyl creosol (p. 500) and methyl eugenol, on oxidation with potassium permanganate. It is the so-called *veratric acid*,  $C_9H_{10}O_4$ , which occurs together with *veratrin* (see the alkaloids) in the *sabadilla* seeds (from *Veratrum Sabadilla*). It crystallizes from hot water in needles, melting at  $179.5^\circ$ . Heated to  $150^\circ$  with hydrochloric acid, it splits off a methyl group and affords the two monomethyl compounds. When digested with lime or baryta it decomposes into  $CO_2$  and dimethyl-pyrocatechin (p. 496).

*Diethylprotocatechuic acid* melts at  $149^\circ$ .

*Monomethyl-protocatechuic Acids*,  $C_8H_8O_4$  :—



The first body is *vanillic acid*, obtained by the energetic oxidation of its aldehyde, *vanillin* (and from *coniferine*, p. 521), also from *aceteugenol*, *acetferulic acid*, and from *aceto-homovanillic acid* when oxidized with potassium permanganate (p. 560). It crystallizes from hot water in shining needles, melts at  $211^\circ$ , and can be sublimed. When it is heated to  $150^\circ$  with hydrochloric acid it decomposes into methyl chloride and protocatechuic acid; distilled with lime it yields *guaiacol*. When methylated it is converted into dimethyl-protocatechuic acid, from which it is again regained by a partial demethylation.

Isomeric monomethyl-protocatechuic acid (formula 2),—*Isovanillic Acid*,—was first obtained from *hemipinic acid*, and is prepared together with *vanillic acid* by methylating protocatechuic acid, or by demethylating dimethyl-protocatechuic acid, and by oxidizing *hesperitinic acid*. It melts at  $250^\circ$ .

*Coniferyl alcohol* (p. 521), *eugenol* and *ferulic acid*, stand in close relation to *vanillic acid*; they contain unsaturated side-chains, and, therefore, are treated in connection with the *cinnamic acid* derivatives. *Meconine*, *opianic acid* and *hemipinic acid* bear close genetic relation; they are included under the dibasic acids.

The methylene ether of protocatechuic acid is

*Piperonylic Acid*,  $C_8H_6O_4 = C_6H_3 \left( \begin{matrix} O \\ O \end{matrix} \right) CH_2.CO_2H$ , Methylene-protocatechuic acid, is formed upon oxidizing its aldehyde, *piperonal* (p. 521), with po-

tassium permanganate. It is prepared synthetically by heating protocatechuic acid with methylene iodide and potassium hydroxide, and can be decomposed conversely into protocatechuic acid and carbon on heating with hydrochloric acid. It sublimes in fine needles, melting at  $228^{\circ}$ , and is with difficulty soluble in hot water. Heated to  $210^{\circ}$  with water it breaks up into pyrocatechin,  $\text{CO}_2$  and carbon.

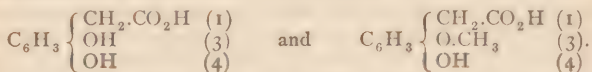
Ethylene-protocatechuic acid is a perfect analogue of piperonylic acid. It is prepared by means of ethylene bromide, and melts at  $133^{\circ}$ .

Ether derivatives of protocatechuic acid and the trivalent phenol, phloroglucin (p. 501), are:—**Luteolin**, **Maclurin**, and **Catechin**. The first,  $\text{C}_{20}\text{H}_{10}\text{O}_8$ , occurs in *Reseda luteola* and crystallizes in yellow needles. Ferric chloride colors it green. When fused with potassium hydroxide it is resolved into protocatechuic acid and phloroglucin:—



The second and third bodies are generally included among the tannic acids. They also are decomposed into protocatechuic acid and phloroglucin on fusion with potassium hydroxide.

We must yet mention **Homo-protocatechuic Acid**,  $\text{C}_8\text{H}_8\text{O}_4$ , and **Homo-vanillic Acid**,  $\text{C}_9\text{H}_{10}\text{O}_4$ :—

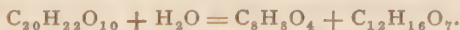


The latter is produced (along with vanillic acid, in the careful oxidation of acetugenol,  $\text{C}_6\text{H}_3(\text{C}_3\text{H}_5)$ )  $\left\{ \begin{smallmatrix} \text{O} \cdot \text{CH}_3 \\ \text{O} \cdot \text{C}_2\text{H}_5\text{O} \end{smallmatrix} \right.$ . It melts at  $142^{\circ}$ , and when heated with hydrochloric acid yields homo-protocatechuic acid, melting at  $127^{\circ}$ .

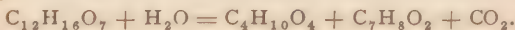
## 2. Acids, $\text{C}_8\text{H}_8\text{O}_4$ .

**Orsellinic Acid**,  $\text{C}_6\text{H}_2(\text{CH}_3) \left\{ \begin{smallmatrix} (\text{OH})_2 \\ \text{CO}_2\text{H} \end{smallmatrix} \right.$ . Orsellic or lecanoric acid,  $\text{C}_{16}\text{H}_{14}\text{O}_7 + \text{H}_2\text{O}$ , is found in different mosses of the varieties *Roccella* and *Lecanora*. It can be extracted from the same by means of ether or milk of lime. Its crystals are almost perfectly insoluble in water, melt at  $153^{\circ}$ , and are colored red by ferric chloride. Boiling with lime changes it to *orsellinic acid*,  $\text{C}_8\text{H}_8\text{O}_4$ . The latter consists of easily soluble prisms, and is colored violet by ferric chloride. It melts at  $176^{\circ}$ , and decomposes into  $\text{CO}_2$ , and orcin,  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH})_2$  (p. 498).

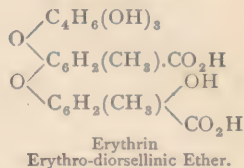
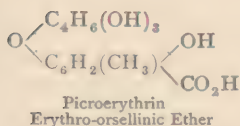
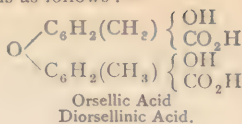
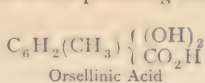
**Erythrin**,  $\text{C}_{20}\text{H}_{22}\text{O}_{10}$  (Erythrinic Acid), is an ether-like derivative of orsellinic acid and erythrite,  $\text{C}_4\text{H}_6(\text{OH})_4$  (p. 369). It occurs in the lichen *Roccella fusciformis*, which is applied in the manufacture of archil (p. 499) and is extracted from it by means of milk of lime. Erythrin crystallizes with  $1\frac{1}{2}$  molecules  $\text{H}_2\text{O}$ , and is difficultly soluble in hot water. Exposure to the air causes it to assume a red color. When it is boiled with water or baryta-water it breaks up into orsellinic acid or picroerythrin:—



**Picro-erythrin**,  $\text{C}_{12}\text{H}_{16}\text{O}_7 + \text{H}_2\text{O}$ , forms crystals, which dissolve readily in alcohol and ether, and on further boiling with baryta water yield erythrite, orcin and  $\text{CO}_2$ :—



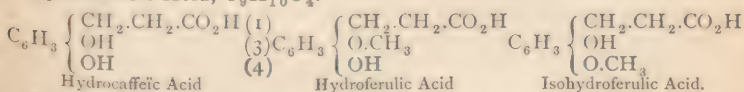
The structure of the preceding compounds is as follows :—



### 3. Acids, $\text{C}_9\text{H}_{10}\text{O}_4$ .

**Hydro-umbellic Acid**,  $\text{C}_9\text{H}_8(\text{OH})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  (1, 2, 4 —  $\text{CH}_2$  in 1). The position of its side-chains is the same as in  $\beta$ -resorcylic acid (p. 558). It is obtained from umbellic acid,  $\text{C}_9\text{H}_8\text{O}_4$ , and umbelliferon,  $\text{C}_9\text{H}_6\text{O}_3$  (see this), by the action of sodium amalgam. Above  $110^\circ$  it decomposes, water separating, and melts at  $120^\circ$ . Ferric chloride colors it green. It reduces alkaline copper and silver solutions. It yields resorcinol on fusion with KOH.

### **Hydrocaffeic Acid**, $\text{C}_9\text{H}_{10}\text{O}_4$ .



The hydrocaffeic acid, with the same arrangement of side-chains as in protocathechuic acid, is obtained from caffeic acid by the action of sodium amalgam; is colored the same by ferric chloride, etc., as the protocathechuic acid (p. 559), and reduces both alkaline copper and silver solutions. **Hydroferulic** and **Isohydroferulic Acids** are its monomethyl ethers. They correspond to vanillic and isovanillic acids. Sodium amalgam converts ferulic and isoferulic acids into the above hydro-acids. The former melts at  $90^\circ$ , the latter at  $147^\circ$  (*Ber.*, 14, 965).

**Evernic Acid**,  $\text{C}_9\text{H}_{10}\text{O}_4$ , is produced, together with orsellinic acid, on boiling *evernic acid*,  $\text{C}_{17}\text{H}_{16}\text{O}_7$  (from *Evernia Prunastri*), with baryta. It melts at  $157^\circ$ , and is colored violet by ferric chloride.

### **Dioxy-alcoholic Acids**, $\text{C}_9\text{H}_{10}\text{O}_4$ .



The  $\alpha$ -acid (**Atroglyceric Acid**) results on boiling dibrom-hydro-atropic acid (p. 545) with excess of alkalies, and from benzoyl carbinol (p. 510) by means of CNH and hydrochloric acid (*Ber.*, 16, 1292). It crystallizes from water in warty masses, and melts at  $146^\circ$ .

The  $\beta$ -Acid (**Phenylstyeric Acid**) is obtained from dibromhydrocinnamic ester (p. 544) by first getting the dibenzoyl ester and saponifying it, or by boiling phenyl- $\alpha$  chlorolactic acid and the two phenyloxyacrylic acids (p. 557) with water (together with phenylacetaldehyde). It is a crystalline mass, very soluble in water, and melts about  $117^\circ$ , with partial decomposition.



## MONOBASIC TRIOXYACIDS.

**Gallic Acid**,  $C_7H_6O_5 = C_6H_2(OH)_3.CO_2H$  (1, 3, 4, 5 —  $CO_2H$  in 1), a trioxybenzoic acid, occurs free in gall nuts, in tea, in the fruit of *Cæsalpinia coriaria* (Divi-divi), in mangoes, and in various other plants. When combined, and then chiefly as a glucoside, it occurs in some tannic acids. It is obtained from the ordinary tannic acid (tannin) by boiling it with dilute acids. It is prepared artificially on heating di-iodo-salicylic acid to  $130^\circ$  with potassium carbonate, and from brom-dioxy-benzoic acid, brom-proto-catechuic and veratric acids (p. 559) when fused with potassium hydroxide.

Gallic acid arises, like pyrogallol carboxylic acid (below), from the *adjacent* trioxybenzene (pyrogallol). Since the carboxyl in the latter occupies the ortho-position referred to a hydroxyl, and since but 2 pyrogallol acids are possible, gallic acid would then be the second isomide (*Ber.*, 17, 1090).

Gallic acid crystallizes in fine, silky needles,  $C_7H_6O_5.H_2O$ . It dissolves in 3 parts of boiling, and 130 parts of water at  $12^\circ$ , and readily in alcohol and ether. It has a faintly acid, astringent taste. It melts and decomposes near  $220^\circ$ , into  $CO_2$ , and pyrogallol,  $C_6H_3(OH)_3$ . It reduces both gold and silver salts (hence its application in photography). Ferric chloride throws down a blackish-blue precipitate in its solutions.

Although gallic acid is monobasic, it can, by virtue of its being a trivalent phenol, combine also to salts with four equivalents of metal. The solutions of the alkali salts absorb oxygen when exposed to the air, and, in consequence, become brown in color.

Gallic acid forms a *triacetate*,  $C_6H_2(O.C_2H_3O)_3.CO_2H$ , with acetyl chloride. This crystallizes from alcohol in needles. The *ethyl ester*,  $C_6H_2(OH)_3.CO_2.C_2H_5$ , crystallizes with  $2\frac{1}{2}$  molecules  $H_2O$  and is soluble in water. When it is anhydrous it melts at  $150^\circ$ , and sublimes. *Triethyl-gallate*,  $C_6H_2(O.C_2H_5)_3.CO_2H$ , from gallic acid, melts at  $112^\circ$ , and forms an easily soluble barium salt (*Ber.*, 17, 1090).

*Rufigallic Acid*,  $C_{14}H_8O_8$ , a derivative of anthracene (see this), is obtained by heating gallic acid with four parts of sulphuric acid to  $140^\circ$ .

Oxidizing agents, such as arsenic acid, silver oxide, iodine and water, convert gallic into *Ellagic Acid*,  $C_{14}H_8O_9$ . The latter occurs in the bezoar stones (an intestinal calculus of the Persian goat). It is obtained from this source by boiling with potassium hydroxide, and precipitating with hydrochloric acid. Ellagic acid separates out in the form of a powder containing 1 molecule of  $H_2O$ , and is insoluble in water.

**Pyrogallol-carboxylic Acid**,  $C_6H_2(OH)_3.CO_2H$  (1, 2, 3, 4— $CO_2$  in 1), is isomeric with gallic acid, and is prepared by heating pyrogallol with ammonium carbonate. It is more difficultly soluble in water, crystallizes in shining needles containing  $\frac{1}{3}H_2O$ , and sublimes without decomposition in a current of  $CO_2$ . Ferric chloride colors it violet and greenish-brown; it also reduces alkaline copper and silver solutions. *Triethyl-pyrogallol-carboxylic acid*,  $C_6H_2(O.C_2H_5)_3.CO_2H$ , crystallizes in long, shining needles, and melts at  $100.5^\circ$ . It also results in the oxidation of triethyldaphnetic acid (vide this). It yields triethyl pyrogallol by the elimination of  $CO_2$  (p. 501).

An isomeric trioxyethylbenzoic acid,  $C_6H_2(O.C_2H_5)_3.CO_2H$ , has also been obtained from æsculetin. It melts at  $134^\circ$  (*Ber.*, 16, 2113).

## TANNIC ACIDS.

The tannins or tannic acids are substances widely disseminated in the vegetable kingdom. They are soluble in water, possess an acid, astringent taste, are colored dark blue or green (ink) by ferric salts, precipitate gelatine and enter into combination (leather) with animal hides (gelatine). Hence they are employed in the manufacture of leather, and for the preparation of ink. They are precipitated from their aqueous solutions by neutral acetate of lead.

Some tannic acids appear to be glucosides of gallic acid, *i. e.*, ethereal compounds of the same with various sugars. They decompose into gallic acid and grape sugar upon boiling with dilute acids. Others contain phloroglucin,  $C_6H_3(OH)_3$ , instead of grape sugar. Common tannic acid, tannin, appears to be, at least in a pure state, not a glucoside but a digallic acid.

When the tannic acids are fused with KOH they yield mostly protocatechuic acid and phloroglucin.

**Tannic Acid, Tannin,  $C_{14}H_{10}O_9 + 2H_2O$ , Digallic Acid,** occurs in large quantity (upwards of 50 per cent.), in gall nuts (pathological concretions upon the different oak species, *Quercus infectoria*, produced by the sting of insects); in sumach (*Rhus coriaria*), in tea and other plants. It is prepared artificially by oxidizing gallic acid with silver nitrate, by heating it with  $POCl_3$  to  $130^\circ$ , and by boiling with dilute arsenic acid. Conversely, it passes, on boiling with dilute acids or alkalies, into gallic acid (without the appearance of sugar):—



Pure tannin must, therefore, be considered a digallic acid (*Ber.*, 17, 1478).

Tannin is best obtained from gall-nuts. The latter are finely divided and extracted with ether and alcohol. The solution separates into two layers, the lower of which is aqueous and contains tannin chiefly, and this is obtained by evaporation (see *Zeitschrift für analyt. Chemie*, 11, 367).

Pure tannic acid is a colorless, shining, amorphous mass, very soluble in water, but little in alcohol, and almost insoluble in ether. Many salts (*e. g.*, sodium chloride) precipitate it from its aqueous solutions, and it can also be removed from the latter with ether. It reacts acid and is colored dark-blue by ferric chloride; gelatine precipitates it. Quantitative methods of estimating tannin are based on this behavior.

The acid generally forms salts with two equivalents of metal; these are obtained pure with difficulty. Acetic anhydride converts the acid into a *penta-acetate*,  $C_{14}O_5(C_2H_3O)_5O_9$ . Heated to  $210^\circ$  it decomposes with formation of pyrogallol,  $C_6H_3(OH)_3$ .

The other tannic acids found in plants have been but little investigated : we may mention :—

*Kino-tannin*, which constitutes the chief ingredient of kino, the dried juice of *Pterocarpus erinaceus* and *Coccoloba uvifera*. Its solution is colored green by ferric salts. It yields phloroglucin on fusion with potassium hydroxide.

*Catechu-Tannin* occurs in catechin, the extract of *Mimosa Catechu*. Ferric salts color it a dirty-green (p. 559). *Catechin* or *Catechinic Acid*,  $C_{21}H_{20}O_8 + 5H_2O$ , is also present in catechu. It crystallizes in shining needles (*Ber.*, 13, 695).

*Moringa-Tannin*,  $C_{13}H_{10}O_6 + H_2O$ , *Maclurin*, is found in yellow wood (*Morus tinctoria*) from which it may be extracted (along with morin) with hot water. When the solution cools morin separates out; maclurin is precipitated from the concentrated liquid by hydrochloric acid, in the form of a yellow crystalline powder, soluble in water and alcohol. Ferric salts impart a greenish-black color to its solutions. When fused with KOH it yields protocatechuic acid and phloroglucin.

*Morin*,  $C_{13}H_8O_6 + 2H_2O$ , decomposes into phloroglucin and resorcin. Nitric acid oxidizes it to  $\beta$ -resorcylic acid.

The *Tannin of Coffee*,  $C_{30}H_{18}O_{16}$ , occurs in coffee beans and Paraguay tea. Gelatine does not precipitate its solutions. Ferric chloride gives them a green color. It decomposes into caffeic acid (see this) and sugar, when boiled with potassium hydroxide. Fusion with KOH produces protocatechuic acid.

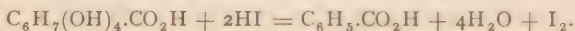
The tannin of oak is found in the bark (together with gallic acid, ellagic acid, quercite, synanthrose). It has the formula  $C_{19}H_{16}O_{10}$ , and is a red powder, not very soluble in cold water, but more readily in acetic ether. Ferric chloride colors its solution dark blue. Boiling, dilute sulphuric acid converts it into the so-called *oak-red* (phlobaphene),  $C_{38}H_{26}O_{17}$  (*Ber.*, 16, 2710).

The *Tannin* found in the quinine barks is combined with the quinia-alkaloids. It closely resembles ordinary tannic acid, but is colored green by ferric salts. When boiled with dilute acids it breaks up into sugar and *quina-red*, an amorphous brown substance, yielding protocatechuic acid and acetic acid on fusion with KOH.

**Quinic Acid**,  $C_7H_{12}O_6$ , is a *tetra-oxy-monocarboxylic acid*. It is present in the cinchona barks, in coffee beans, in bilberry and many other plants. It is obtained as a secondary product in the preparation of quinine, by extracting the quinia bark with dilute sulphuric acid and precipitating the alkaloids with milk of lime. When the filtered solution is evaporated the calcium salt of the acid separates out.

The acid consists of rhombic prisms, and dissolves very easily in water, but with difficulty in strong alcohol. The aqueous solution is lævo-rotatory. It melts at  $162^\circ$ , and upon further heating decomposes into hydroquinone, pyrocatechin, benzoic acid, phenol and other products. Oxidizing agents ( $MnO_2$  and sulphuric acid) convert it into formic acid,  $CO_2$  and quinone. Ferments decompose it into propionic acid, acetic acid and formic acid. It is a monobasic acid and furnishes easily soluble salts. The *calcium salt*,  $(C_7H_{11}O_6)_2Ca + 10H_2O$ , crystallizes in rhombic leaflets, which effloresce on exposure to the air.

Quinic acid is reduced by hydriodic acid to benzoic acid:—



Phosphoric chloride converts it into chlor-benzoic chloride:—



Acetic anhydride will convert its ethyl ester into tetracetyl-ethyl ester,  $\text{C}_6\text{H}_7(\text{O} \cdot \text{C}_2\text{H}_3\text{O})_4 \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$ , which yields large crystals, melting at  $135^\circ$ . Hence, quinic acid is to be looked upon as a hydrogen addition product of a tetra-oxy-benzoic acid:  $\text{C}_6\text{H}(\text{H})_6 \left\{ \begin{array}{l} (\text{OH}) \\ \text{CO}_2\text{H} \end{array} \right\}_4$ . It passes into protocatechuic acid on fusion with potassium hydroxide.

## DIBASIC ACIDS.

**Acids,  $\text{C}_8\text{H}_6\text{O}_4 = \text{C}_6\text{H}_4 \begin{array}{c} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{array}$ .**

1. **Phthalic Acid,  $\text{C}_8\text{H}_6\text{O}_4$** , is the ortho-dicarboxylic acid of benzene, and was first obtained by oxidizing naphthalene and chlorinated naphthalenes with nitric acid. It also results on oxidizing ortho-xylene and ortho-toluic acid with potassium permanganate, alizarin and purpurin with nitric acid, or with  $\text{MnO}_2$  and sulphuric acid; and in slight amount in the oxidation of benzene and benzoic acid. It is very difficult to get it by using chromic acid as an oxidizing agent, since the latter is very apt to burn it at once to  $\text{CO}_2$  (p. 528).

*Preparation.*—Boil naphthalene tetrachloride,  $\text{C}_{10}\text{H}_8\text{Cl}_4$ , with 10 parts nitric acid (sp. gr. 1.45) until perfect solution is reached. Naphthalene tetrachloride is obtained by adding a mixture of naphthalene (2 parts) and  $\text{KClO}_3$  (1 part) to crude hydrochloric acid (11 parts). (*Ber.*, 11, 735).

Phthalic acid crystallizes in short prisms or in leaflets, which dissolve readily in hot water, alcohol and ether. It melts at  $184^\circ$  (*Ann.*, 200, 271), and when further heated decomposes into phthalic anhydride and water. When heated with an excess of calcium hydroxide it yields benzene and  $2\text{CO}_2$ . Only  $1\text{CO}_2$  is split off and calcium benzoate produced (p. 531) if its lime salt be heated to  $330\text{--}350^\circ$  with 1 molecule of  $\text{Ca}(\text{OH})_2$ . Barium chloride added to aqueous ammonium phthalate precipitates barium phthalate, which is very difficultly soluble in water.

$\text{PCl}_5$  converts phthalic acid into **phthalyl chloride,  $\text{C}_6\text{H}_4(\text{CO} \cdot \text{Cl})_2$** . In accord with all its transpositions this appears to have the constitution  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CCl}_2 \\ \text{CO} \end{array} \text{O}$ . Zinc and hydrochloric acid convert it into phthalid (p. 552), and with benzene and  $\text{AlCl}_3$ , or with mercury diphenyl, it yields  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{C}_6\text{H}_5)_2 \\ \text{CO} \end{array} \text{O}$ , phthalophenone, and with zinc ethyl,

*Phthalyl-ethyl,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{C}_2\text{H}_5)_2 \\ \text{CO} \end{array} \text{O}$* , is produced. The latter combines with hydroxylamine (*Ber.*, 17, 817). This reagent converts phthalyl chloride into the



same *phthalyl-hydroxamic acid*,  $C_6H_4 \begin{smallmatrix} \diagup C(N.OH) \\ \diagdown CO \end{smallmatrix} O$ , melting at  $230^\circ$ , as is obtained from phthalic anhydride. It is a liquid, boiling at  $268^\circ$ , and reverting to phthalic acid when boiled with water. The esters derived from phthalic chloride differ from those derived from phthalic acid (*Ber.*, 16, 860). Sodium amalgam converts phthalyl chloride (unlike other transformations) into phthalyl alcohol (p. 509).

**Phthalic Anhydride**,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$  (see p. 316), is obtained by distilling phthalic acid or digesting it with acetyl chloride. It crystallizes in long, prismatic needles, melting at  $128^\circ$ , and boiling at  $277^\circ$ . It yields phthalyl-hydroxamic acid (*Ber.*, 16, 1781), with hydroxylamine. It also readily affords various condensation products, *e. g.*, with the fatty acids (p. 548), and benzene hydrocarbons (see benzoyl benzoic acid), and with the phenols it yields the important phthalein dye-substances. See *Ber.*, 17, 1389, for its condensations with aceto-acetic and malonic esters.

*Dihydrophthalic Acid*,  $C_8H_8O_4$ , results from the action of sodium amalgam upon the aqueous solution of phthalic acid and soda. The acid crystallizes in plates, dissolves readily in hot water and alcohol, and melts at about  $200^\circ$ , with decomposition into phthalic anhydride, water and hydrogen. Benzoic acid results through oxidation, or by the action of concentrated sulphuric acid.

*Tetrahydrophthalic Acid*,  $C_8H_{10}O_4$ , is obtained when its anhydride is heated with water. The anhydride results in distilling isohydropyromellitic acid (p. 570); it crystallizes in leaflets, and melts at  $68^\circ$ . The acid is very soluble in water, crystallizes in leaflets, and melts at  $96^\circ$ , with decomposition into water and the anhydride.

**2. Isophthalic Acid**,  $C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown CO_2H \end{smallmatrix}$  (1, 3), is obtained: by oxidizing isoxylene and isotoluic acid with a chromic acid mixture; by fusing potassium meta-sulphobenzoate, meta-brombenzoate and benzoate with potassium formate (terephthalic acid is also formed in the last two cases); by the action of the ester of chlorcarbonic acid and  $HgNa$  upon meta-dibrombenzene; from meta-dicyanbenzene (p. 526); also by heating hydro-pyromellitic and hydrophrenitic acid (p. 570), and by oxidizing colophony with nitric acid. Iso-phthalic acid crystallizes from hot water in fine, long needles. It is soluble in 460 parts boiling, and 7800 parts cold water. It melts above  $300^\circ$ , and sublimes in needles.

The *barium salt*,  $C_8H_4O_4Ba + 3H_2O$ , crystallizes in fine needles, and is very soluble in water; therefore, it is not precipitated by barium chloride from a solution of ammonium isophthalate (distinction between phthalic and terephthalic acids).

The *Dimethyl-isophthalate*,  $C_6H_4(CO_2.CH_3)_2$ , crystallizes from alcohol in needles, and melts at  $65^\circ$ . The *ethyl ester* is liquid, solidifies below  $0^\circ$ , and boils at  $285^\circ$ .

**3. Terephthalic Acid**,  $C_6H_4(CO_2H)_2$  (1, 4), was first obtained by oxidizing turpentine oil. It results in oxidizing paraxylene.

paratoluic acid and all di-derivatives of benzene having two carbon chains belonging to the para-series (*e. g.*, cymene and cumene) with chromic acid. The oxidation of crude xylene affords terephthalic (15 per cent.) and isophthalic (85 per cent.) acids, which are separated by means of their barium salts. Terephthalic acid is produced, too, when paradicyanbenzene,  $C_6H_4(CN)_2$  (p. 526), is boiled with alkalis. The best course to pursue in forming terephthalic acid is to oxidize caraway oil (a mixture of cymene and cuminol) with chromic acid.

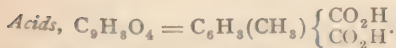
Terephthalic acid is a powder, which is almost perfectly insoluble in water, alcohol and ether, and is, therefore, precipitated from its salts by acids. It sublimes without previous fusion when it is heated. Sometimes terephthalic acid is obtained with properties slightly different from the regular acid (insoluble acid). The cause of this seems to be due to an admixture of acetophenone-carboxylic acid (*Ber.*, 12, 1074).

The calcium salt,  $C_8H_4O_4Ca + 3H_2O$ , and barium salt,  $C_8H_4O_4Ba + 4H_2O$ , are very difficultly soluble in water. The methyl ester,  $C_8H_4(CH_3)_2O_4$ , melts at  $140^\circ$ ; the ethyl ester, at  $44^\circ$ ; both crystallize in prisms.

Sodium amalgam converts terephthalic acid in alkaline solution into hydro-terephthalic acid,  $C_8H_8O_4$ , a white powder, insoluble in water.

Sulpho-terephthalic Acid,  $C_6H_3(SO_3H)(CO_2H)_2$ , is only dibasic (*Ber.*, 14, 223).

Nitro-terephthalic Acid,  $C_8H_5(NO_2)O_4$ , melts at  $270^\circ$ .



Uvic Acid, Mesidic Acid (1, 3, 5), is obtained by oxidizing mesitylene,  $C_6H_3(CH_3)_3$ , with dilute nitric acid (mesitylenic acid is produced at the same time, p. 542). It is formed synthetically by boiling pyroracemic acid with baryta water (p. 410). It crystallizes from hot water in needles, melting at  $287^\circ$ . Chromic acid oxidizes it to trimesic acid (p. 569); distilled with lime it at first yields metatoluic acid, then toluene (p. 531).

Xylidic Acid  $C_6H_3(CH_3)_3(CO_2H)_2$ , is obtained by oxidizing pseudocumene,  $C_6H_3(CH_3)_3$  (1, 3, 4), xylic acid and so-called paraxylic acid with dilute nitric acid; hence its structure is (1, 3, 4— $CH_3$  in 3) (p. 542). Potassium permanganate oxidizes it to trimellitic acid. Boiling water separates it in flocculent masses; it melts at  $282^\circ$  and sublimes.



Phenyl-Succinic Acid,  $\begin{array}{c} | \\ CH_2 \cdot CO_2H \end{array} = C_{10}H_{10}O_4$ , results from

$\alpha$  chlorstyrene,  $C_6H_5 \cdot C_2H_3Cl$ , by means of potassium cyanide; by the decomposition of phenyl acetsuccinic ester, by means of alkalis; from phenyl-carboxysuccinic acid (p. 570), and from the so-called hydro-cornicularic acid,  $C_{17}H_{16}O_3$ . It crystallizes from hot water in warty masses, melts at  $167^\circ$  ( $162^\circ$ ) and (like succinic acid) yields an anhydride,  $C_{10}H_8O_3$ , melting at  $45-50^\circ$ .

**$\beta$ -Phenylisosuccinic Acid**,  $C_6H_5.CH_2.CH(CO_2H)_2$ , Benzyl Malonic Acid, formed from sodium malonic ester,  $CH(Na)(CO_2R)_2$ , and benzyl chloride, melts at  $117^\circ$ , and at  $180^\circ$  decomposes into  $CO_2$  and hydrocinnamic acid,  $C_6H_5.CH_2.CH_2.CO_2H$ .

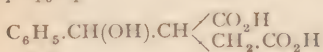
### OXYDICARBOXYLIC ACIDS AND OXYALDEHYDIC ACIDS.

The oxydicarboxylic acids,  $C_6H_3(OH).(CO_2H)_2$ , can be obtained from the dicarboxylic acids by the introduction of the OH-group, by means of the amido- or sulpho-derivatives. They are also formed from the oxy-monocarboxylic acids,  $C_6H_4(OH).CO_2H$ , by heating their alkali salts in a current of  $CO_2$ , or by means of the  $CCl_4$  reaction (p. 530). Their ether acids, *e. g.*,  $C_6H_3(O.CH_3).(CO_2H)_2$ , result on the oxidation of the ether acids of the oxytoluic acids,  $C_6H_3(O.CH_3) \begin{smallmatrix} < \\ CH_3 \\ CO_2H \end{smallmatrix}$  (p. 552), and by the same treatment of the *oxyaldehydic acids*,

$C_6H_3(O.CH_3) \begin{smallmatrix} < \\ CHO \\ CO_2H \end{smallmatrix}$  (the latter are obtained from the oxymonocarboxylic acids,  $C_6H_4(OH).CO_2H$ , by means of the  $CCl_3H$  reaction, and by further introduction of methyl); when the phenol ethers are heated with hydrochloric acid the free oxydicarboxylic acids result. Hence, the six possible **Oxyphthalic Acids**,  $C_6H_3(OH).(CO_2H)_2$ , can be obtained by these reactions (*Ber.*, 16, 1966).

The so-called **Oxyuvitic Acid**,  $C_7H_8O_5 = C_6H_2(CH_3) \begin{smallmatrix} \{ OH \\ (COOH)_2 \end{smallmatrix}$ , is a homologue of the oxydicarboxylic acids, and is produced by the action of chloroform, chloral or trichloroacetic ester upon sodium aceto-acetic ester (p. 410). It crystallizes from hot water in fine needles, and melts under decomposition at about  $290^\circ$ .

**Phenyl-itamalic Acid**,  $C_{11}H_{12}O_5$ , and **Phenyl-paraconic Acid**,  $C_{11}H_{10}O_4$ .



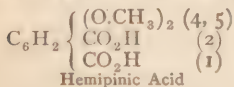
Phenyl-itamalic Acid



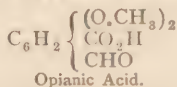
Phenyl-paraconic Acid.

The first is a  $\gamma$ -oxy acid, therefore, when in a free condition it at once decomposes into  $H_2O$  and its lactone—phenyl-paraconic acid (p. 364). The second is obtained on heating benzaldehyde with sodium succinate and acetic anhydride (p. 576). It crystallizes from hot water in shining needles, and melts at  $99^\circ$ . When it is boiled with alkalis it yields the salts of phenyl-itamalic acid. Upon heating, phenyl-paraconic acid decomposes into  $CO_2$ , phenyl-butyrolactone (p. 557) and isophenyl-crotonic acid (*Ann.*, 216, 113, *Ber.*, 17, 415).

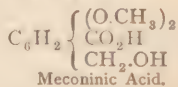
The *dioxy-derivatives*, which are closely related to protocatechuic acid and methyl vanillin (p. 521), are *hemipinic acid*,  $C_{10}H_{10}O_6$ , *opianic acid*,  $C_{10}H_{10}O_5$ , *meconinic acid*,  $C_{10}H_{12}O_5$ , and *meconine*,  $C_{10}H_{10}O_4$  :—



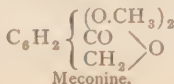
Hemipinic Acid



Opianic Acid.



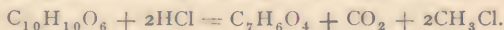
Meconinic Acid.



Meconine.

These compounds are obtained by oxidizing narcotine with dilute nitric acid or with manganese peroxide and sulphuric acid.

**Hemipinic Acid**,  $C_{10}H_{10}O_6$ . We must consider this a carboxyl derivative of dimethyl protocatechuic acid, since it decomposes, when heated with hydrochloric acid, into protocatechuic acid,  $CO_2$  and methyl chloride:—



When it is heated with soda-lime it breaks up into  $2CO_2$  and dimethylpyrocatechin (p. 496). It crystallizes from hot water in large prisms, containing water of crystallization. In an anhydrous state it melts at  $182^\circ$ , and yields an anhydride, melting at  $167^\circ$ . Hence, the  $CO_2H$  groups occupy the ortho-position.

**Opianic Acid**,  $C_{10}H_{10}O_5$ , is an aldehyde-dimethyl-protocatechuic acid, because when it is heated with hydrochloric acid it yields protocatechuic aldehyde,  $CO_2$  and two molecules of methyl chloride. It is converted into dimethyl-protocatechuic aldehyde (p. 521) when heated with soda-lime. It crystallizes from hot water in fine prisms, melting at  $140^\circ$ . It is oxidized to hemipinic acid. When acted upon with hydrochloric or hydriodic acid at elevated temperatures the two methyl groups split off, and we obtain **Noropianic Acid**,  $C_6H_2(OH)_2(CHO).CO_2H$ , which melts at  $171^\circ$ ; isovanillin is formed simultaneously by the breaking off of  $CO_2$  and a methyl group.

**Meconine**,  $C_{10}H_{10}O_4$ , results when  $HgNa$  acts upon opianic acid and the solution is precipitated by acids. At first the sodium salt of **Meconinic Acid**,  $C_{10}H_{12}O_5$ , is produced. The latter is a  $\gamma$ -oxyacid, and at once parts with water, passing into its lactone anhydride—meconine (see Phthalid, p. 552). Meconine occurs already formed in opium, and is obtained on boiling narcotine with water. It yields shining crystals, melting at  $110^\circ$ , and dissolving with difficulty in water. It dissolves in the alkalis, yielding salts of meconinic acid.

## TRIBASIC ACIDS.

*Benzene Tricarboxylic Acids*,  $C_6H_3(CO_2H)_3$ , 3 isomerides.

1. **Trimesic Acid**,  $C_9H_6O_6$  (1, 3, 5), is formed when mesitylenic and uvitic acids are oxidized with a chromic acid mixture (mesitylene is at once burnt up); by heating mellitic acid with glycerol (together with tetracarboxylic acids), or hydro- and isohydromellitic acid with sulphuric acid. It crystallizes in short prisms, which dissolve readily in hot water and alcohol. It melts about  $300^\circ$ , and sublimes near  $240^\circ$ . Heated with lime it decomposes into  $3CO_2$  and benzene.

The sodium salt,  $C_9H_5NaO_6$ , is very difficultly soluble in water. The neutral barium salt,  $(C_9H_3O_6)_2Ba_3 + H_2O$ , is insoluble in water. Barium chloride precipitates the primary salt,  $(C_9H_5O_6)_2Ba + 4H_2O$ , from the solution of the ammonium salt. The triethyl ester,  $C_6H_3(CO_2.C_2H_5)_3$ , crystallizes in silky prisms, melting at  $129^\circ$ .

2. **Trimellitic Acid**,  $C_6H_3(CO_2H)_3$  (1, 2, 4). This is obtained (together with isophthalic acid) by heating hydro-pyro-mellitic acid with sulphuric acid, or upon oxidizing xylic acid with potassium permanganate. It is prepared most readily (along with isophthalic acid) by oxidizing colophony with nitric acid (*Ann.*, 172, 97), is very soluble in water, and separates in warty masses. It melts at  $216^\circ$ , decomposing into water and the anhydride,  $C_6H_2(CO_2H)(CO)_2O$ . The latter melts at  $158^\circ$ .



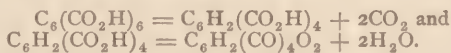
3. **Hemimellitic Acid**,  $C_6H_3(CO_2H)_3$  (1, 2, 3). This is formed on heating hydromellophanic acid (below) with sulphuric acid. It affords needles, which are difficultly soluble in water, melts at  $185^\circ$ , and decomposes into phthalic anhydride and benzoic acid.

**Phenyl-ethenyl-tricarboxylic Acid**,  $C_6H_5 \cdot CH(CO_2H) \cdot CH(CO_2H)_2$  (vide p. 366), or **Phenyl-carboxy-succinic Acid**, is obtained from phenylchloroacetic ester,  $C_6H_5 \cdot CHCl \cdot CO_2R$ , by the action of sodium malonic ester,  $CHNa(CO_2R)_2$ . It is a crystalline mass, easily soluble in water, and at  $191^\circ$  decomposes into  $CO_2$  and phenyl succinic acid (p. 567).

### TETRABASIC ACIDS.

*Benzene Tetracarboxylic Acids*,  $C_6H_2(CO_2H)_4$ . There are three isomerides.

1. **Pyromellitic Acid**,  $C_{10}H_6O_8$ . Its anhydride is produced when mellitic acid is distilled, or better, when the sodium salt is subjected to the same treatment with sulphuric acid ( $1\frac{1}{2}$  parts):—



The acid results when the anhydride is boiled with water.

Pyromellitic acid is very similar to phthalic acid. It crystallizes in prisms containing  $2H_2O$ , and dissolves readily in hot water and alcohol. At  $100^\circ$  it loses its water of crystallization, melts at  $264^\circ$ , and decomposes into water and the *dianhydride*,  $C_{10}H_2O_6$ , which sublimes in long needles, and melts at  $286^\circ$ .

Hydro- and iso-hydro-pyro-mellitic acids,  $C_{10}H_{10}O_8 = C_6H_2(H_4)(CO_2H)_4$ , are obtained by the continued action of sodium amalgam upon the aqueous solution of the ammonium salt. The first results as a gummy mass upon evaporating the ethereal solution; it is very soluble in water. The second crystallizes with  $2H_2O$ , loses the same about  $120^\circ$ , melts near  $200^\circ$ , and decomposes into water,  $CO_2$  and tetrahydrophthalic anhydride (p. 566). When heated with sulphuric acid both evolve  $CO_2$  and  $SO_2$  and form trimellitic and isophthalic acids.

2. **Phrenitic Acid**,  $C_{10}H_6O_8$ , results (together with mellophanic acid and trimesic acid) upon heating hydro- and isohydro-mellitic acid (p. 571) with sulphuric acid. It is very soluble in water, and crystallizes in warty masses containing  $2H_2O$ , and melting at  $238^\circ$ . Its salts crystallize with difficulty.

Sodium amalgam acting upon the ammonium salt solution, produces *Hydro-phrenitic acid*,  $C_{10}H_{10}O_8$ , an amorphous, very soluble mass, which yields phrenitic acid and isophthalic acid when it is heated with sulphuric acid.

3. **Mellophanic Acid**,  $C_6H_2(CO_2H)_4$ , is formed together with phrenitic acid from hydro- and isohydromellitic acid, and is an ill-defined, anhydrous compound, melting at  $215\text{--}238^\circ$ , with separation of water. Sodium amalgam converts it into an hydro-acid.

### HEXABASIC ACIDS.

**Mellitic Acid**,  $C_{12}H_6O_{12} = C_6(CO_2H)_6$ . This occurs in *mellite* or *honey-stone*, which is found in some lignite beds. Honey-stone is an aluminium salt of mellitic acid,  $C_{12}Al_2O_{12} + 18H_2O$ , and affords large quadratic pyramids of a bright yellow color.

In preparing the acid, honeystone is boiled with ammonium carbonate, ammo-

nium hydroxide added, and the separated aluminium hydroxide filtered off. The ammonium salt,  $C_{12}(NH_4)_6O_{12} + 9H_2O$ , crystallizes from the filtrate in large rhombic prisms, which effloresce in the air. The free acid is obtained by conducting chlorine into the aqueous solution of the ammonium salt (*Ber.*, 10, 560).

An interesting formation of mellitic acid is that whereby pure carbon (graphite, charcoal, etc.) is oxidized with an alkaline solution of potassium permanganate. Another is when the carbon is applied as positive electrode in electrolysis (*Ber.*, 16, 1209).

Mellitic acid crystallizes in fine, silky needles, readily soluble in water and alcohol. It is very stable, and is not decomposed by acids, by chlorine or bromine, even upon boiling. When heated it melts and decomposes into water,  $CO_2$ , and pyromellitic anhydride. It yields benzene when distilled with lime.

Mellitic acid forms salts with six equivalents of metal. The *calcium* and *barium*,  $C_{12}Ba_3O_{12} + 3H_2O$ , salts are insoluble in water. The *methyl ester*,  $C_6(CO_2.CH_3)_6$ , crystallizes in leaflets, melting at  $187^\circ$ ; the *ethyl ester* melts at  $73^\circ$ .  $PCl_5$  produces chloranhydrides.

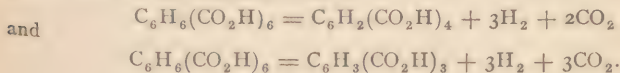
The known amides of mellitic acid are *Paramide* and *Euchroic Acid*; they appear in the dry distillation of the ammonium salt.

*Paramide* or *Mellimide*,  $C_{12}H_3N_3O_6 = C_6 \left( \begin{smallmatrix} CO \\ CO \end{smallmatrix} \right) (NH)_3$ , is a white, amorphous powder, insoluble in water and alcohol. Heated to  $200^\circ$  with water, it is converted into the tertiary ammonium salt of mellitic acid. The alkalis convert paramide into euchroic acid.

*Euchroic Acid*,  $C_{12}H_4N_2O_8 = C_6 \left( \begin{smallmatrix} CO \\ CO \end{smallmatrix} \right) (NH)_2 \left\{ \begin{smallmatrix} CO.OH \\ CO.OH \end{smallmatrix} \right\}$ , crystallizes in large prisms, and is difficultly soluble in water. Heated with water to  $200^\circ$  it yields mellitic acid. Nascent hydrogen changes euchroic acid to *euchrone*, a dark blue precipitate, which reverts to colorless euchroic acid upon exposure. Euchrone dissolves with a dark red color in alkalis.

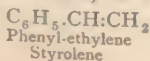
Sodium amalgam acting on ammonium mellitate produces *Hydromellitic Acid*,  $C_{12}H_6(H_6)O_{12}$ . This is very soluble in water and alcohol, difficultly in ether, and is indistinctly crystalline. It melts under decomposition. It is hexabasic, its calcium salt being more soluble in cold than in hot water. If the acid be heated to  $180^\circ$  with concentrated hydrochloric acid, or if it be preserved, it is transformed into the isomeric *Isohydromellitic Acid*,  $C_{12}H_{12}O_{12}$ , crystallizing in large, six-sided prisms. Hydrochloric acid precipitates it from its aqueous solution.

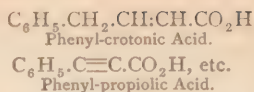
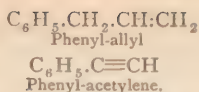
When more highly heated with sulphuric acid, both acids yield phrenitic acid, mellophanic acid and trimesic acid:—



## UNSATURATED COMPOUNDS.

The benzene derivatives previously studied contain saturated side-chains, having carbon present in them. Perfectly analogous compounds exist, in which unsaturated side-chains are present:—





Hydrogen converts them into the corresponding saturated compounds.

### Hydrocarbons.

**Styrolene, Phenyl Ethylene**,  $\text{C}_8\text{H}_8 = \text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}_2$ , Vinyl benzene, Cinnamene, occurs in storax (p. 576) (1-2 per cent.), from which it is obtained upon distillation with water. It is prepared by heating cinnamic acid with lime or with water to  $200^\circ$  (cinnamene); by the action of alcoholic potash upon brom-ethyl benzene (p. 416), and by the condensation of acetylene,  $\text{C}_2\text{H}_2$ , upon application of heat. It is best obtained from  $\beta$ -brom-hydro-cinnamic acid (p. 543), which is immediately decomposed by a soda solution into styrolene,  $\text{CO}_2$  and  $\text{HBr}$  (*Ber.*, **15**, 1983). It is a mobile, strongly refracting liquid, with an agreeable odor. The styrolene from liquid storax is optically active; this, however, seems to be caused by impurities. Artificial, pure styrolene is optically inactive and boils at  $144\text{--}145^\circ$ ; its sp. gr. = 0.925 at  $0^\circ$ .

Styrolene changes upon standing, more rapidly on application of heat, into *metastyrolene*, an amorphous non-transparent mass, yielding styrolene again when distilled. Another polymeride, distyrolene, obtained by heating styrolene with sulphuric acid, boils at  $310^\circ$  (*Ann.*, **216**, 187). A second distyrolene is produced in the distillation of calcium cinnamate, and melts at  $117^\circ$ .

Hydriodic acid converts styrolene into ethyl benzene,  $\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5$ ; chromic acid or nitric acid oxidizes it to benzoic acid.

Being an unsaturated compound, styrolene can directly take up two halogen atoms. The *chloride*,  $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$  (p. 416), is a liquid; the *bromide*,  $\text{C}_6\text{H}_5\cdot\text{Br}_2$ , formed by adding bromine to hot ethyl benzene, crystallizes in leaflets or needles, melting at  $69^\circ$ ; the iodide is unstable.

Two series of mono-substitution products result when the hydrogen of the side-chain of styrolene suffers replacement:—



The  $\alpha$ -products are derived (along with phenylacetaldehyde) from the phenyl- $\alpha$  chlor (brom-) lactic acid (p. 556), upon heating with water. They are oils having a hyacinth-like odor, boil undecomposed, and are far less reactive than the  $\beta$ -products (similar to the halogen propylenes, p. 74).  $\alpha$  **Chlor-styrolene**,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CHCl}$ , is obtained from  $\alpha$ -dichlor-ethyl-benzene (p. 416), and boils at  $199^\circ$ .  $\alpha$  **Brom-styrolene** is formed from dibrom-cinnamic acid (p. 544), by boiling with water or digesting with a soda-solution. It melts at  $7^\circ$  and boils at  $220^\circ$ . When it is heated with water it yields phenyl-acetaldehyde,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CHO}$  (p. 103).

The  $\beta$ -products result on heating styrolene chloride (-bromide),  $\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_3\text{Cl}_2$ , alone, with lime or with alcoholic potash. They do not distil undecomposed, and possess a penetrating odor, causing tears. They afford acetophenone,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3$  (*Ber.*, **14**, 323), when they are heated with water (to  $180^\circ$ ) or with sulphuric acid.  $\beta$  **Chlor-styrolene**,  $\text{C}_6\text{H}_5\cdot\text{CCl}:\text{CH}_2$ , also results from

$\beta$ -dichlorethyl benzene (p. 416), when it is digested with alcoholic potash.  $\beta$ -Brom-styrolene yields phenyl acetylene with alcoholic potash at  $120^\circ$ ; sodium and  $\text{CO}_2$  convert it into phenyl-propionic acid.

#### Nitro-styrolenes.

$\alpha$ -Nitro-styrolene,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}(\text{NO}_2)$ , is obtained by boiling styrolene with fuming nitric acid, by heating benzaldehyde to  $190^\circ$  with nitromethane,  $\text{CH}_3(\text{NO}_2)$ , and  $\text{ZnCl}_2$  (*Ber.*, 16, 2591), and by the action of fuming nitric acid upon phenyl-isocrotonic acid (*Ber.*, 17, 413). It possesses a peculiar odor, provoking tears, is readily volatilized in aqueous vapor, and yields yellow needles, melting at  $58^\circ$ . It is oxidized to benzoic acid.

The nitro-styrolenes,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CH}:\text{CH}_2$  (o-, m- and p), containing the nitro-group in the benzene nucleus, result from the nitrophenyl- $\beta$ -brom-lactic acids (from the three nitro-cinnamic acids, p. 556), by the action of a soda solution in the cold, or upon boiling the  $\beta$ -lactones obtained from the phenyl-brom-lactic acids with water (*Ber.*, 16, 2213, 17, 595). **Orthonitro-styrolene** melts at  $13^\circ$ , has a peculiar odor, and is colored blue by sulphuric acid. **Meta-nitro-styrolene** melts at  $-5^\circ$ , **para-nitro-styrolene** at  $29^\circ$ ; both have an odor like that of cinnamic aldehyde.

**o-Nitro-chlor-styrolene**,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CH}:\text{CHCl}$ , is produced in the preparation of o-nitro-phenyl chlor-lactic acid (p. 556) and melts at  $59^\circ$  (*Ber.*, 17, 1070).

**Dinitro-styrolene**,  $\text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{CH}:\text{CH}(\text{NO}_2)$ , results from p-a-dinitro-cinnamic acid (p. 579), by the splitting-off of  $\text{CO}_2$ ; it consists of yellow leaflets, melting at  $199^\circ$ . When it is heated to  $100^\circ$  with sulphuric acid it is broken up into p-nitrobenzaldehyde, CO and hydroxylamine (*Ber.*, 16, 849).

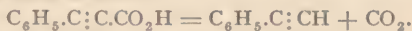
#### Amido-styrolenes.

**o-Amido-chlor-styrolene**,  $\text{C}_6\text{H}_4(\text{NH}_2)\cdot\text{CH}:\text{CHCl}$ , is obtained by reducing o-nitro-phenyl chlor-styrolene (see above) with tin and hydrochloric acid; it consists of white prisms. Heated to  $170^\circ$  with sodium alcoholate it yields indol,  $\text{C}_8\text{H}_7\text{N}$ .

**p-Amido-styrolene**,  $\text{C}_6\text{H}_4(\text{NH}_2)\cdot\text{CH}:\text{CH}_2$ , is produced (together with p-amido-cinnamic acid), in the reduction of p-nitro-cinnamic ester; it melts about  $81^\circ$ .

See *Ann.*, 218, 374, upon phenyl-propylenes,  $\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_5$ , allyl benzenes, etc.

**Phenyl Acetylene**,  $\text{C}_6\text{H}_5\cdot\text{C}:\text{CH}$ , acetenyl benzene, is produced when  $\beta$ -brom-styrolene and acetophenone chloride,  $\text{C}_6\text{H}_5\cdot\text{CCl}_2\cdot\text{CH}_3$ , are heated to  $130^\circ$  with alcoholic potash; also from phenyl-propionic acid (p. 581), on heating it with water to  $120^\circ$ , or upon distilling the barium salt:—



It is a pleasant-smelling liquid, boiling at  $139\text{--}140^\circ$ . It forms metallic compounds, like acetylene, with ammoniacal silver and copper solutions:  $(\text{C}_6\text{H}_5)_2\text{Cu}_2$  is bright yellow,  $(\text{C}_6\text{H}_5)_2\text{Ag}_2 + \text{Ag}_2\text{O}$  is white. The sodium compound,  $\text{C}_6\text{H}_5\text{Na}$ , inflames in the air, and with  $\text{CO}_2$  it yields propionic acid. When phenyl-acetylene is dissolved in sulphuric acid and diluted with water, it yields acetophenone (see p. 521).

**o-Nitrophenyl Acetylene**,  $\text{C}_6\text{H}_4\begin{smallmatrix} \diagup \text{C}:\text{CH} \\ \diagdown \text{NO}_2 \end{smallmatrix}$ . This is produced on boiling orthonitro-phenylpropionic acid with water. It forms needles, melting at  $81\text{--}82^\circ$ , and yields metallic compounds with Cu and Ag.



**p-Nitrophenyl Acetylene**,  $C_6H_4(NO_2).C:CH$ , from paranitro-phenylpropionic acid, melts at  $152^\circ$ .

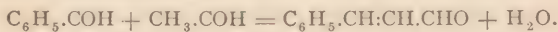
**o-Amidophenyl Acetylene**,  $C_6H_4(NH_2)C:CH$ , is produced in the reduction of orthonitrophenyl-acetylene with zinc dust and ammonia, or with ferrous sulphate and potassium hydroxide, and in the decomposition of amido-phenylpropionic acid. It is an oil with an odor resembling that of the indigo vat. Sulphuric acid and water convert it into ortho-amido-acetophenone (p. 523).

**Phenyl-diacetylene**,  $C_6H_5.C:C.C:C_6H_5$ . This arises on shaking the copper derivative of phenyl acetylene in the air (with some ammonia) or more readily by the action of alkaline potassium ferricyanide (*Ber.*, 15, 57). It crystallizes from alcohol in long needles, melting at  $97^\circ$ , combines with eight atoms of bromine and does not afford metallic derivatives. *It is the parent hydrocarbon of indigo-blue*. Its ortho-dinitro-derivative,  $C_6H_4 \begin{smallmatrix} C:C.C:C \\ NO_2O_2N \end{smallmatrix} C_6H_4$ , obtained from ortho-nitro-phenyl acetylene copper, by means of alkaline potassium ferricyanide and melting at  $212^\circ$ , yields isomeric *disatogene*,  $C_{16}H_{18}N_2O_4$  (comp. p. 582), with sulphuric acid. Ammonium sulphide at once converts this into indigo-blue,  $C_{16}H_{10}N_2O_2$  (*Ber.*, 15, 53).

#### Alcohols and Aldehydes.

**Styryl Alcohol**,  $C_9H_{10}O = C_6H_5.CH:CH.CH_2.OH$  (Styrene, Cinnamyl Alcohol), is obtained by saponifying styracine, its cinnamic ester, with potassium hydroxide. It crystallizes in shining needles, is difficultly soluble in water, possesses a hyacinth-like odor, melts at  $33^\circ$ , and distils at  $250^\circ$ . When carefully oxidized it becomes cinnamic acid, but in case the oxidation is energetic, benzoic acid is the product. In the presence of platinum sponge it oxidizes in the air to cinnamic aldehyde. It yields cinnamic ether  $(C_9H_9)_2O$ —a mobile oil—when it is digested with boric anhydride.

**Cinnamic Aldehyde**,  $C_9H_8O$ , is the chief ingredient of the essential oil of cinnamon and cassia (from *Persea Cinnamomum* and *Persea Cassia*). It is obtained by the oxidation of cinnamic alcohol, by dry distillation of a mixture of calcium cinnamate and formate, and by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid:—



This reaction is in all particulars like that of the condensation of aldehyde to crotonaldehyde (p. 159).

To obtain the aldehyde from cinnamon oil, shake the latter with a solution of primary sodium sulphite, wash the crystals which separate with alcohol, and decompose them with dilute sulphuric acid.

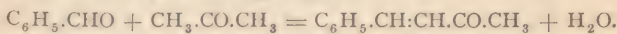
Cinnamic aldehyde is a colorless, aromatic oil, which sinks in water and boils at  $247^\circ$ ; it distils readily in aqueous vapor. When exposed to the air it oxidizes to cinnamic acid, and in other respects shows all the properties of the aldehydes. Dry ammonia converts it into the crystalline base **Hydro-cinnamide**,  $(C_9H_8)_3N_2$  (p. 521).

Its *Phenylhydrazine* compound,  $C_6H_5.CH:CH.CH(N_2H.C_6H_5)$ , melts at  $168^\circ$ .

**o-Nitrocinnamic Aldehyde**,  $C_6H_4(NO_2).CH:CH.CHO$ . The condensation in the cold of ortho-nitrobenzaldehyde with acetaldehyde, by means of dilute sodium hydroxide, affords at first **o-Nitrophenyl-lactic aldehyde**,  $C_6H_5(NO_2).CH(OH).CH_2.CHO$  (p. 512). When this is boiled with acetic anhydride it yields ortho-nitrocinnamic aldehyde (*Ber.*, 16, 2205). The latter crystallizes in colorless needles, and melts at  $127^\circ$ .

### Ketones.

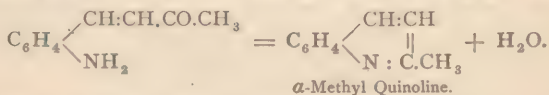
**Benzylidene Acetone**,  $C_6H_5.CH:CH.CO.CH_3$ , Benzyl Acetone, Cinnamyl-methyl ketone, is obtained on distilling calcium cinnamate and acetate. It is very easily procured by the condensation of benzaldehyde with acetone (p. 512) on shaking with dilute sodium hydroxide (*Ann.*, 223, 139):—



It separates as a thick oil, which solidifies after distillation. It has a peculiar odor, crystallizes in brilliant quadratic plates, melts at  $41-42^\circ$ , and boils near  $262^\circ$ . It dissolves in sulphuric acid with an orange-red color, and combines with sodium bisulphite.

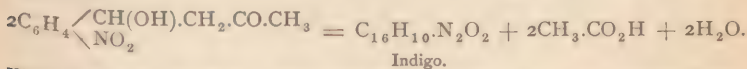
The nitration of benzalacetone with sulphuric acid and nitric acid in the cold affords the ortho- and para-nitro-derivatives; these can be separated by means of alcohol (*Ber.*, 16, 1954).

**o-Nitrobenzal Acetone**,  $C_6H_4(NO_2).CH:CH.CO.CH_3$ , forms warty crystals, melting at  $59^\circ$ . The action of alcoholic potash, hydrochloric acid, and then sodium hydroxide produces *indigo* (see below).  $\alpha$ -Methyl quinoline results from it by reduction with stannous chloride and hydrochloric acid (p. 541 and p. 517):



**p-Nitrobenzal Acetone** melts at  $254^\circ$  (*Ber.*, 16, 1970).

If dilute sodium hydroxide be allowed to act upon a mixture of ortho-nitrobenzaldehyde with acetone we first get (by aldol condensation) **o-Nitrophenyl-lactic-methyl Ketone**,  $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$ , melting at  $69^\circ$ , which is at once transformed by more sodium hydroxide (by union of 2 molecules and elimination of 2 molecules of acetic acid) into *indigo* (Baeyer, *Ber.*, 15, 2857):—



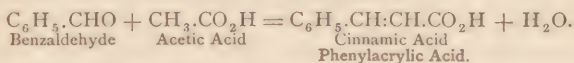
When it is boiled with acetic anhydride water splits off and it is converted into ortho-nitrobenzylidene acetone (see above).

In a like manner para-nitrobenzaldehyde yields, with acetone and sodium hydroxide, **p-Nitrophenyl-lactic-methyl Ketone** (melting at  $58^\circ$ ). If this be boiled with acetic anhydride it yields para-nitrobenzal acetone (*Ber.*, 16, 1968).

**Dibenzylidene Acetone**,  $C_6H_5.CH:CH \searrow CO$  (**Cinnamone**), is produced by the condensation of benzylidene acetone (see above) with benzaldehyde, caused by the action of sodium hydroxide in alcoholic solution. It crystallizes in bright yellow needles, and melts at  $112^\circ$ .

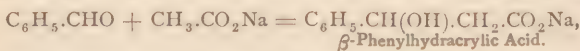
*Acids.*

In addition to the general methods for preparing aromatic acids (p. 529) and for the conversion of saturated into unsaturated acids (p. 189), we can also prepare the unsaturated aromatic acids synthetically, by a method of very general applicability. It is based upon the condensation of aromatic aldehydes with the fatty acids (p. 155), effected by heating with the chlorides of the acids, *e. g.*,  $\text{CH}_3\text{COCl}$  (Bertagnini), or with the free acids in the presence of zinc chloride or hydrochloric acid (Schiff):—

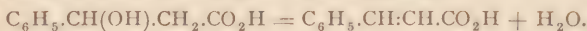


or, better, with a mixture of the sodium salts and the anhydrides of the fatty acids (Perkin).

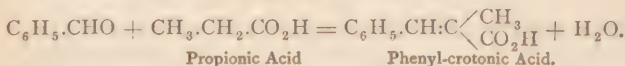
In the last case the reaction occurs between the aldehyde and the sodium salt (*Ber.*, 14, 2110), when, by the aldol condensation, we obtain a  $\beta$ -oxyacid:—



which is then deprived of water by the acid anhydride:—



All aromatic aldehydes (aldehyde phenols, aldehydic acids), react similarly with the homologous fatty acids and with many other compounds (p. 512). Thus, phenyl-crotonic acid,  $\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_4\cdot\text{CO}_2\text{H}$ , is produced from benzaldehyde by means of the sodium salt and the anhydride of propionic acid, and the coumaric acids,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{C}_2\text{H}_2\cdot\text{CO}_2\text{H}$ , etc., from the oxybenzaldehydes,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CHO}$ , with acetic acid. With the higher fatty acids the condensation occurs in such a manner that the two hydrogen atoms are withdrawn from the carbon atom in union with carboxyl (*Ann.*, 204, 187, and 208, 121):—



Similarly, phenyl-paraconic acid (p. 568), and (by withdrawal of  $\text{CO}_2$ ) isophenyl-crotonic acid (p. 581) are obtained from benzaldehyde with sodium succinate and acetic anhydride. Benzalmalonic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{C}(\text{CO}_2\text{H})_2$ , and cinnamic acid are formed from benzaldehyde and malonic acid. Glacial acetic acid may be employed instead of acetic anhydride (*Ber.*, 16, 1436, 2516).

**Cinnamic Acid**,  $\text{C}_9\text{H}_8\text{O}_2 = \text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , phenylacrylic acid (*Acidum cinnamylicum*), occurs in Peru and Tolu balsams (p. 532), in storax and in some benzoïn resins. It results in the oxidation of its aldehyde or its alcohol, by the condensation of benzaldehyde with sodium acetate, by the decomposition of benzal malonic acid, etc.

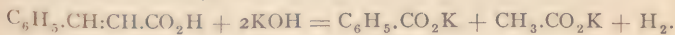
Cinnamic acid is obtained either synthetically from benzaldehyde, or from storax (*Styrax officinalis*)—the pressed-out, thick sap of the bark of *Liquidambar*

*orientale*. This contains, besides a resin, some free cinnamic acid and styrolene,  $C_8H_8$ , but chiefly *styracine* (cinnamic cinnamate and phenyl-propylic cinnamate p. 500). The styrolene is distilled off upon boiling with water. The residue is boiled with a soda solution, in order to remove the cinnamic acid; cold alcohol will extract the resin from what remains and only styracine is left. To obtain the cinnamic acid, storax is boiled for some time with sodium hydroxide, when the cinnamyl alcohol which is formed will distil over. Hydrochloric acid precipitates cinnamic acid from the solution. It is purified by distillation or crystallization from benzene (comp. *Ann.*, 188, 194.)

To get the acid from benzaldehyde, a mixture of the latter (3 parts) with sodium acetate (3 parts) and acetic anhydride (10 parts), is boiled for several hours, water then added and the acid dissolved in soda (*Ber.*, 10, 68). A more convenient procedure consists in heating benzalchloride,  $C_6H_5.CHCl_2$  (1 part) with sodium or potassium acetate (2 parts) to 180–200°.

Cinnamic acid crystallizes from hot water in fine needles, from alcohol in thick prisms, is odorless, melts at 133°, and when quickly heated distils near 300° with almost no decomposition. It is soluble in 3500 parts water of 17°, and readily in hot water.

The cinnamates are similar to the benzoates; ferric chloride produces a yellow precipitate in their solutions. In chemical character cinnamic acid closely resembles the acids of the acrylic acid series. Fusion with KOH decomposes it into benzoic and acetic acids (p. 190):—



Nitric acid and chromic acid oxidize it to benzaldehyde and benzoic acid. When heated with water to 180–200°, or with lime, it breaks up into  $CO_2$  and styrolene. The acid of distyrene,  $C_{17}H_{16}O_2$ , and distyrolene (p. 572) are produced on heating with sulphuric acid.

The *ethyl ester* of cinnamic acid,  $C_9H_7O_2(C_2H_5)$ , is a liquid, boiling at 271°. It readily combines with bromine (dissolved in  $CS_2$ ) to form the dibromide,  $C_9H_7Br_2O_2.C_2H_5$ , melting at 69°. The *methyl ester* melts at 33.5°, and boils at 263°. Cinnamein, contained in Tolu and Peru balsams, consists of benzylic benzoate and cinnamate. It is obtained artificially by heating sodium cinnamate with benzylic chloride. It possesses an aromatic odor, crystallizes from alcohol in small, shining prisms, melting at 39°, and boiling about 320°.

Styracine, present in storax, is the cinnamic ester of cinnamyl alcohol,  $C_8H_7.CO.O.C_9H_9$  (p. 574). It is best obtained from storax, by digesting the latter at 30° with dilute sodium hydroxide, until the residue (styracine) becomes colorless. It crystallizes from hot alcohol in fine needles, melting at 44°, and decomposes when distilled.

As cinnamic acid is unsaturated it is capable of taking two additional affinities. Hydrogen converts it into hydrocinnamic acid; chlorine affords dichlor-, bromine dibrom-hydrocinnamic acid (cinnamic dibromide), and HBr and HI convert it into  $\beta$ -brom- and iodo-hydro-cinnamic acids (p. 543). ClOH changes it to phenyl- $\alpha$ -chlor-lactic acid (p. 556).

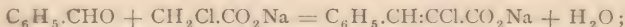
#### Halogen Cinnamic Acids.



Both are obtained from  $\alpha\beta$ -dichlorhydrocinnamic acid (p. 543) by the action of alcoholic potash, and may be separated by means of their potassium salts (*Ber.*, 15, 788).



**$\alpha$ -Chlor-cinnamic Acid** is produced synthetically in the condensation of sodium chloracetate, when heated to  $110^{\circ}$ , with acetic anhydride (*Ber.*, 15, 1945):—



and from phenyl- $\alpha$  chlorlactic acid (p. 556) by the withdrawal of water on heating with acetic anhydride (*Ber.*, 16, 854). It melts at  $142^{\circ}$  ( $139^{\circ}$ ); its alkali salts are very readily soluble in water.

**$\beta$ -Chlor-cinnamic Acid** melts at  $114^{\circ}$ ; upon distillation it suffers a very slight transposition.

The brom-cinnamic acids are prepared like the chlor-cinnamic acids, by boiling the  $\alpha,\beta$ -dibrom-hydro-cinnamic acid with alcoholic potassium hydroxide. They can be separated by means of their ammonium salts, or by the fractional precipitation of the salt mixture (*Ann.*, 154, 146).

**$\alpha$ -Brom-cinnamic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CBr}\cdot\text{CO}_2\text{H}$ , whose  $\text{NH}_4$ -salt is difficultly soluble, and which is first precipitated, crystallizes from hot water in fine needles, melting at  $131^{\circ}$ , and then sublimes. Its *ethyl ester* boils at  $290^{\circ}$ .

**$\beta$ -Brom-cinnamic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , whose alkali salts are deliquescent, crystallizes from hot water in shining leaflets, melting at  $121^{\circ}$ . It changes to the  $\alpha$ -acid if heated with hydriodic acid, and if distilled or heated for some time to  $150$ – $180^{\circ}$ . It sustains a like transposition if converted into its ethers by alcohol and hydrochloric acid; the ester of the  $\alpha$ -acid is then formed. Both acids yield phenyl-propionic acid when boiled with alcoholic potassium hydroxide.

The halogen cinnamic acids (o-, m-, and p-), having the substitutions in the benzene nucleus, are obtained from the three diazocinnamic acids,  $\text{C}_6\text{H}_4(\text{N}_2\text{X})\cdot\text{C}_2\text{H}_2\cdot\text{CO}_2\text{H}$ , when they are digested with the haloid acids, and in this way all nine chlor-, brom-, and iodo-cinnamic acids,  $\text{C}_6\text{H}_4\text{X}\cdot\text{C}_2\text{H}_2\cdot\text{CO}_2\text{H}$ , have been prepared (*Ber.*, 15, 2301, 16, 2040).

#### *Nitro-cinnamic Acids*, $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ .

The introduction of cinnamic acid into nitric acid of specific gravity 1.5 leads to the formation of the ortho- (60 per cent.), and para-nitro acids, of which the former is the more easily soluble in hot alcohol. To separate them cover the acid mixture with 8–10 parts absolute alcohol, and conduct HCl gas rapidly into the liquid, until complete solution ensues. On cooling the para-ether separates. The mother liquor is evaporated, and the ortho-ether recrystallized from ether (*Ann.*, 212, 122, 150). The esters are saponified with sodium carbonate, or by heating with a mixture of 10 parts sulphuric acid, water and glacial acetic acid (equal parts), to  $100^{\circ}$ , or with water and sulphuric acid (*Ann.*, 221, 265).

The three isomeric acids can be prepared from the corresponding nitro-benzaldehydes by means of sodium acetate, etc. (p. 576) (*Ber.*, 14, 830).

**o-Nitro-cinnamic Acid** is insoluble in water, crystallizes from alcohol in needles, melting at  $240^{\circ}$ , and sublimes with partial decomposition. It colors concentrated sulphuric acid dark blue upon warming. Chromic acid oxidizes it to nitro-benzoic acid and potassium permanganate converts it into ortho-nitrobenzaldehyde (p. 515). Bromine unites with it with difficulty, yielding the di-

bromide,  $C_6H_4(NO_2).CHBr.CHBr.CO_2H$ , melting at  $180^\circ$ , and forming ortho-nitrophenylpropionic acid (p. 581), and then isatin when digested with sodium hydroxide. Indol results upon heating it with sodium hydroxide and zinc dust.

The *ethyl ester* of ortho-nitrocinnamic acid is very soluble in cold alcohol, crystallizes in needles or prisms, and melts at  $44^\circ$ . It yields carbostyryl (p. 580), if digested with aqueous ammonium sulphide, and oxy-carbostyryl if the solution be alcoholic. Tin and hydrochloric acid reduce it to ortho-amidocinnamic ester (p. 580), and zinc dust and hydrochloric acid to hydrocarbostyryl (p. 541). The ester readily unites with bromine, yielding the dibromide,  $C_6H_4(NO_2).CHBr.CHBr.CO_2.C_2H_5$ , melting at ( $110^\circ$ )  $71^\circ$  (*Ann.*, 212, 130), and serving for the preparation of ortho-nitrophenylpropionic acid (p. 581).

*m*-Nitro-cinnamic Acid has been obtained from meta-nitrobenzaldehyde, and consists of bright, yellow needles, melting at  $197^\circ$ . Oxidation changes it to meta-nitrobenzoic acid; its ethyl ester melts at  $79^\circ$ .

*p*-Nitro-cinnamic Acid (see above), crystallizes from alcohol in shining prisms, and melts at  $286^\circ$ . Chromic acid oxidizes it to para-nitrobenzoic acid, while sulphuric and nitric acid convert it into para-nitrobenzaldehyde (p. 516). Its *ethyl ester* is almost insoluble in cold alcohol and ether, forms fine needles, and melts at  $138^\circ$ .

*p*- $\alpha$ -Dinitro-cinnamic Acid,  $C_6H_4(NO_2).CH:C(NO_2).CO_2H$ , is obtained from para-nitrocinnamic acid by the action of sulphuric and nitric acids at  $-10^\circ$ . It is very unstable, and at  $0^\circ$  decomposes into  $CO_2$  and dinitrostyrolene (p. 573). Its ethyl ester, from para-nitrocinnamic ester, melts at  $110^\circ$ , and upon reduction yields para-amidophenyl alanine (p. 544) (*Ber.*, 16, 850).

#### *Amido-cinnamic Acids.*

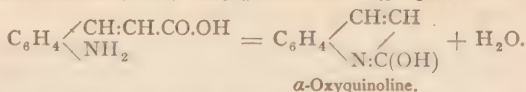
$\alpha$ -Amido-cinnamic Acid,  $C_6H_5.CH:C(NH_2).CO_2H$ , obtained from benzyl-amido-cinnamic acid (*Ber.*, 17, 1620), is very similar to phenyl-alanine (p. 543), decomposes at  $240^\circ$  with formation of phenyl vinyl-amine,  $C_6H_5.CH:CH(NH_2)$ , and by reduction yields phenyl-alanine.

The amido-cinnamic acids,  $C_6H_4(NH_2).C_2H_2.CO_2H$ , with the substitutions in the benzene nucleus, can be obtained from the three nitro-cinnamic acids by reduction with tin and hydrochloric acid. There is greater advantage in reducing them with iron sulphate in alkaline solution (p. 431).

To prepare the ortho-amido-acid add an excess of ammonia and the ammoniacal solution of ortho-nitrocinnamic acid (5 grs.) to the boiling solution of green vitriol (50 grs.), continue boiling on a sand-bath and let the brownish-black precipitate of ferrous-ferric oxide subside. The solution should smell of ammonia, and be perfectly clear, and pure yellow in color, and if this be not the case add ammonia and apply heat. Concentrated hydrochloric acid is gradually added to the filtered solution of the ammonium salt of the amido-acid, as long as the yellow acid is precipitated (*Ber.*, 15, 2294). For the reduction by means of ferrous sulphate and baryta water, see *Ann.*, 221, 266.

*o*-Amido-cinnamic Acid separates in fine yellow needles, when hydrochloric acid is added to solutions of its salts. It melts at  $158-159^\circ$ , evolving gas. It is readily soluble in hot water, in alcohol and ether; the solutions exhibit a greenish-blue fluorescence.

It yields ortho-coumaric acid when diazotized and boiled with water. The splitting-off of water causes it to pass into its lactim—the so-called carbostyryl ( $\alpha$ -oxyquinoline)—(p. 541):—



This anhydride formation ensues on protracted boiling with hydrochloric acid, more rapidly on heating to  $130^\circ$  with hydrochloric acid, or upon heating the acetyl derivative of the ortho-amido-acid. When the acid is heated alone (unlike the ortho-amido-hydro-cinnamic acid, p. 544) it does not yield an anhydride (similar to ortho-coumaric acid).

The *ethyl ester* was first obtained by reducing ortho-nitro-cinnamic ester with tin and hydrochloric acid in alcoholic solution (*Ber.*, 15, 1422); a simpler method consists in conducting HCl into the alcoholic solution of the free amido acid, evaporating and precipitating the aqueous solution with sodium acetate, when the ether will separate in fine yellow needles, melting at  $77^\circ$ . Its solutions show an intensely yellowish-green fluorescence. If digested at  $90^\circ$  with alcoholic  $\text{ZnCl}_2$  it will yield ethyl-oxy-quinoline (see above); and oxy-quinoline if evaporated with hydrochloric acid.

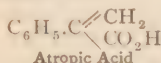
**Ethyl Amido-cinnamic Acid**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CH:CH.CO}_2\text{H} \\ \diagdown \text{NH.C}_2\text{H}_5 \end{array}$ , is obtained when ethyl iodide and potassium hydroxide act upon ortho-amido-cinnamic acid. It melts at  $125^\circ$ , and affords a *nitroso*-body which, by reduction and the splitting-off of  $\text{H}_2\text{O}$ , yields the so-called *quinazol*-compounds (*Ann.*, 221, 285).

The diazo-derivative of the amido-acid unites with sodium sulphite and forms **o-Hydrazin-cinnamic Acid**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}_2\text{H}_2.\text{CO}_2\text{H} \\ \diagdown \text{NH.NH}_2 \end{array}$ , which on application of heat yields **Indazol**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CH} \\ \diagdown \text{NH} \end{array} \text{N}$  (*Ann.*, 221, 280).

**m- and p-Amido-cinnamic Acids**,  $\text{C}_6\text{H}_4.(\text{NH}_2).\text{C}_2\text{H}_2.\text{CO}_2\text{H}$ , are similarly formed from meta- and para-nitrocinnamic acids by reduction with green vitriol and ammonia (*Ber.*, 15, 2299); the first melts at  $181^\circ$ , the second at  $176^\circ$ . The halogen cinnamic acids (p. 540) result upon boiling the diazo-compounds with the haloid acids; and when water is employed meta- and para-coumaric acids result.

**Atropic Acid**,  $\text{C}_9\text{H}_8\text{O}_2$ , is isomeric with cinnamic acid. It results from atropine, tropic acid and atrolactic acid (p. 555) when they are heated with concentrated hydrochloric acid or with baryta water (*Ann.*, 195, 147). It crystallizes from hot water in monoclinic plates, is difficultly soluble in cold water, easily in ether,  $\text{CS}_2$  and benzene; melts at  $106^\circ$ , and distils with aqueous vapor. Chromic acid oxidizes it to benzoic acid; sodium amalgam converts it into hydro-atropic acid, and HCl and HBr change it to  $\alpha$ - and  $\beta$ -halogen hydro-atropic acids (p. 545).

Atropic acid sustains the same relation to cinnamic acid as hydro-atropic to hydro-cinnamic acid or methyl acrylic acid to ordinary crotonic acid (p. 192):—



Like all unsaturated acids when fused with caustic alkali, it splits at the point

of double union, and yields formic and  $\alpha$ -toluic acids,  $C_6H_5 \cdot CH_2 \cdot CO_2H$ , whereas cinnamic acid decomposes into benzoic and acetic acids.

Protracted fusion or heating with water or hydrochloric acid (in small quantity, even upon recrystallization), converts atropic acid into two polymeric *isotropic acids*  $(C_9H_8O_2)_2$  (melting at  $237^\circ$  and  $236^\circ$ ) which are very difficultly soluble, and no longer capable of yielding addition products.

**Phenyl-crotonic Acid**,  $C_{10}H_{10}O_2 = C_6H_5 \cdot CH : C \begin{smallmatrix} \diagup CH_3 \\ \diagdown CO_2H \end{smallmatrix}$ , is obtained from benzaldehyde and propionic acid (comp. p. 576) and by the action of sodium upon benzylic propionate (p. 530). It melts at  $78^\circ$ , and boils at  $288^\circ$ .

**Isophenyl-crotonic Acid**,  $C_6H_5 \cdot CH : CH \cdot CH_2 \cdot CO_2H$ , is produced on heating benzaldehyde with sodium succinate and acetic acid. Phenyl-paraconic acid (p. 568) is produced at first, but this then parts with  $CO_2$ . The acid melts at  $86^\circ$ , and when boiled yields  $H_2O$  and  $\alpha$ -naphthol,  $C_{10}H_7(OH)$ . It unites with  $HBr$ , forming phenyl- $\gamma$ -brombutyric acid, which yields phenyl-butyro-lactone (p. 557) with a soda solution.

**Phenyl-angelic Acid**,  $C_{11}H_{12}O_2 = C_6H_5 \cdot CH : C \begin{smallmatrix} \diagup C_2H_5 \\ \diagdown CO_2H \end{smallmatrix}$ , from benzaldehyde and normal butyric acid, yields **Phenyl-valeric Acid**,  $C_6H_5 \cdot CH_2 \cdot CH(C_2H_5) \cdot CO_2H$ , with sodium amalgam. The ortho-nitro product of this is reduced to an ortho-amido-acid, which parts with water and yields the anhydride,

**ethyl-hydrocarbostyryl**,  $C_{11}H_{13}NO = C_6H_5 \begin{smallmatrix} \diagup CH_2 \cdot CH \cdot C_2H_5 \\ \diagdown NH \cdot CO \end{smallmatrix}$ , which can

be easily changed into  $\beta$ -ethyl-quinoline,  $C_9H_6(C_2H_5)N$  (analogous to the formation of quinoline from ortho-amido-hydrocinnamic acid, p. 544).

We have an example of a doubly unsaturated acid in

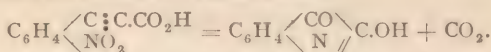
**Phenyl-propionic Acid**,  $C_9H_6O_2 = C_6H_5 \cdot C : C \cdot CO_2H$  (p. 197). It is obtained by boiling  $\alpha$ - and  $\beta$ -brom-cinnamic acids with alcoholic potash, by acting upon phenyl-acetylene sodium,  $C_6H_5 \cdot C : CNa$ , with  $CO_2$ , and when  $CO_2$  and sodium act upon  $\beta$ -brom-styrolene. It is prepared by boiling the dibromide of ethyl cinnamate (p. 577), with alcoholic potash (3 molecules). It crystallizes from hot water or  $CS_2$  in long, shining needles, melting at  $136$ – $137^\circ$  and subliming; under water it melts at  $80^\circ$ . When heated to  $100^\circ$  with water it decomposes into  $CO_2$  and phenyl acetylene. It combines with  $4Br$ , and yields hydrocinnamic acid with  $HgNa$ . When its ethyl ester is dissolved in sulphuric acid and diluted with water we get benzoyl acetic ester (p. 547).

Nitro-phenyl propionic acids,  $C_6H_4(NO_2) \cdot C : C \cdot CO_2H$ .

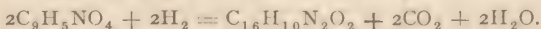
**o-Nitro-phenyl Propionic Acid** is obtained when aqueous soda acts upon the dibromide of ortho-nitro-cinnamic acid. An easier method consists in mixing the dibromide of the ortho-nitro-cinnamic ester (p. 579) with alcoholic potash (3 molecules) (*Ann.*, 212, 140). It occurs in commerce in the form of a 25 per cent. paste. To purify this it is first converted into the ethyl ester. The



acid crystallizes from hot water or alcohol, in needles, or shining leaflets, and decomposes at  $156^{\circ}$ . When boiled with water it decomposes into  $\text{CO}_2$  and ortho-nitrophenyl acetylene (p. 573). When boiled with alkalis it yields isatin:—



It dissolves in concentrated sulphuric acid, with conversion into the isomeric *isatogenic acid*, which at once forms  $\text{CO}_2$  and isatin. *If digested with alkaline reducing agents* (grape sugar and potassium hydroxide, ferrous sulphate, hydrogen sulphide, potassium xanthate) *it readily changes to indigo blue* (Baeyer, 1880):—



Therefore ortho-nitrophenyl propiolic acid may serve as a substitute for natural indigo, especially in calico printing.

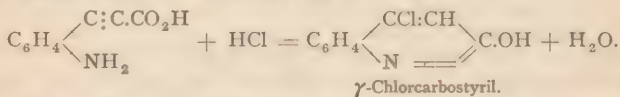
The ethyl ester of the acid is obtained by rapidly conducting  $\text{HCl}$  gas into the mixture of the acid and 10 parts absolute alcohol, until solution ensues. It is very soluble in ether and separates in large crystals, melting at  $60\text{--}61^{\circ}$ . It is saponified on heating a mixture of sulphuric acid, water and glacial acetic acid (equal parts) to 100. (p. 578). When it is dissolved in sulphuric acid it changes to the isomeric isatogenic ester. Ammonium sulphide reduces it to the indoxyl ester.

*p*-Nitrophenyl Propiolic Acid is formed from the para-nitro cinnamic ester, after the same manner as the ortho acid (*Ann.*, 212, 139, 150). It crystallizes from hot alcohol in needles, and melts at  $198^{\circ}$  ( $181^{\circ}$ ) with decomposition. When boiled with water it breaks up into  $\text{CO}_2$  and para-nitrophenyl acetylene. It yields para-nitroacetophenone (p. 523), if digested at  $100^{\circ}$  with sulphuric acid.

The *ethyl ester* crystallizes from alcohol in needles; melting at  $126^{\circ}$ . When digested with sulphuric acid at  $35^{\circ}$  it affords para-nitrobenzoyl acetic acid (p. 547).

**o-Amido-phenyl Propiolic Acid** is obtained by reducing ortho-nitrophenyl propiolic acid with ferrous sulphate and ammonia (*Ber.*, 16, 679). It separates as a yellow, crystalline powder, melting at  $128\text{--}130^{\circ}$ , with decomposition into  $\text{CO}_2$  and ortho-amidophenyl acetylene (p. 574). When boiled with water it yields ortho-amido-acetophenone (p. 523).

$\gamma$ -Chlorcarbostyryl results when the acid is boiled with hydrochloric acid, and  $\gamma$ -oxycarbostyryl upon heating it with sulphuric acid. Here there occurs a closed, ringed-shaped union of atoms (*Ber.*, 15, 2147:—



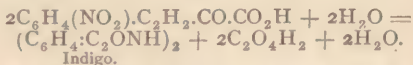
Sodium nitrite converts its  $\text{HCl}$  salt into its diazo-chloride, which at  $70^{\circ}$  yields cinnolin-oxy-carboxylic acid (see this).

*Ketonic Acids* (p. 546).

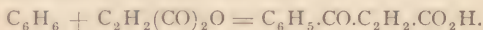
**Cinnamyl Formic Acid**,  $\text{C}_6\text{H}_5\text{.CH:CH.CO.CO}_2\text{H}$ . This is the only unsaturated  $\alpha$ -ketonic acid known. It is obtained, like benzoyl formic acid, from cin-

amic chloride, with CNK, etc.; and by the condensation of benzaldehyde and pyruvic acid,  $\text{CH}_3\text{CO}\cdot\text{CO}_2\text{H}$ , by means of hydrochloric acid gas (p. 512). It is a gummy mass and is gradually decomposed into its components by the alkalis, even in the cold.

The *ortho-nitro derivative* is similarly formed from *ortho-nitrobenzaldehyde*, melts at  $135^\circ$ , and is changed by alkalis, even in the cold, with elimination of oxalic acid, into indigo (*Ber.*, 15, 2863):—



Unsaturated  $\beta$ -ketic acids are produced by the condensation of benzenes with maleic anhydride, etc., by means of  $\text{AlCl}_3$  (see benzoyl propionic acid) (just as phthalic anhydride condenses with fatty acids and benzenes p. 566):—



**Benzoyl Acrylic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , from benzene and maleic anhydride, crystallizes with water in shining leaflets, melting at  $64^\circ$ , but at  $97^\circ$  when anhydrous (*Ber.*, 15, 889). It affords benzoyl propionic acid by reduction (p. 547).

**Benzoyl Crotonic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_3\text{H}_4\cdot\text{CO}_2\text{H}$ , from benzene and citraconic anhydride, melts at  $113^\circ$ .

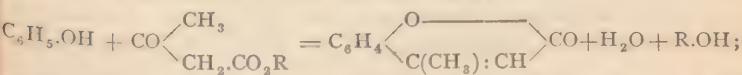
**Benzylidene Aceto-acetic Acid**,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{C} \begin{smallmatrix} \nearrow \text{CO}\cdot\text{CH}_3 \\ \searrow \text{CO}_2\text{H} \end{smallmatrix}$ . Its ethyl ester is formed by the condensation of benzaldehyde and aceto-acetic ester by means of  $\text{HCl}$  or  $\text{ZnCl}_2$ . Sometimes it solidifies in crystalline form, and melts at  $60^\circ$ ; it boils near  $296^\circ$ . Benzaldehyde condenses with ethyl and diethyl aceto-acetic esters, acting at the time upon the methyl group (*Ann.*, 218, 181).

### Oxy-acids.

The unsaturated oxy-acids, or phenol acids, contain hydroxyl in the benzene nucleus, and can be obtained from the unsaturated amido-acids (the amido-cinnamic acids) by boiling the diazo-derivatives with water. They are synthetically prepared from the oxybenzaldehydes,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CHO}$ , by condensation with the sodium salts of the fatty acids (p. 576). Those isomerides, belonging to the *ortho-series*, can here, by exit of water, yield inner anhydrides ( $\delta$ -lactones), called *coumarins*:—

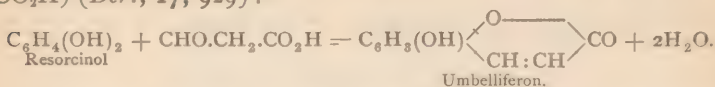


Another synthetic method for the coumarins is the condensation of phenols and aceto-acetic esters when they are heated with sulphuric acid (*Ber.*, 16, 2126; 17, Ref. 138):—



resorcinol especially is very reactive, forming  $\beta$ -methyl umbelliferon.

An analogous reaction is found in the condensation of the phenols with malic acid when heated with sulphuric acid or  $\text{ZnCl}_2$  (it is very probable the malic acid first yields malonic aldehyde,  $\text{CHO}.\text{CH}_2.\text{CO}_2\text{H}$ ) (*Ber.*, 17, 929) :—



*Oxy-phenyl Acrylic Acids*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{OH} \\ \text{CH}:\text{CH}.\text{CO}_2\text{H} \end{array}$ , *Coumaric Acids*.\*

**Meta-coumaric Acid** (1, 3), from meta-amido-cinnamic acid and from meta-oxybenzaldehyde (p. 576), crystallizes from hot water in white prisms, and melts at  $191^\circ$ .  $\text{HgNa}$  converts it into hydro-meta-coumaric acid (p. 554).

**Para-coumaric Acid** (1, 4) is obtained from para-amido-cinnamic acid, and from para-oxybenzaldehyde, also on boiling the extract of aloes with sulphuric acid. It crystallizes from hot water in needles, and melts at  $206^\circ$ . Sodium amalgam converts it into hydropara-coumaric acid; fused with  $\text{KOH}$  it yields para-oxybenzoic acid and acetic acid.

**Ortho-coumaric Acid** (1, 2) occurs in *Melilotus officinalis*, together with hydro-coumaric acid. Nitrous acid converts ortho-amido-cinnamic acid into coumaric acid; its acetyl derivative is obtained from salicylic aldehyde and sodium acetate (*Ber.*, 10, 284) :—



It is most readily prepared by boiling coumarin for some time with concentrated potassium hydroxide.

*Preparation*.—Dissolve 5 grs. of coumarin in 10 grs.  $\text{KOH}$  and 5 grs. water, then boil in a flask until the evolution of hydrogen commences. The fused mass is dissolved in water, precipitated with  $\text{HCl}$  and the coumaric acid separated from the unaltered coumarin by means of a solution of soda.

Ortho-coumaric acid is very easily soluble in hot water and in alcohol, and melts with decomposition at  $202^\circ$ . Sodium amalgam converts it into melilotic acid and fusion with  $\text{KOH}$  into salicylic and acetic acids. Its alkali salt solutions are yellow colored and show a green fluorescence. *Aceto-coumaric acid* (see above) melts at  $146^\circ$ , and is split into acetic acid and coumarin on the application of heat. The free coumaric acid heated alone does not yield coumarin, but only when treated with acetic chloride or anhydride.

In addition to the above ortho-coumaric acid ( $\beta$ ) we have also  $\alpha$ -coumaric acid or the so-called **Coumarinic Acid**,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{OH} \\ \text{C}_2\text{H}_2.\text{CO}_2\text{H} \end{array}$ , which is known only in its salts and ethers, and when set free at once yields water, and its

\* The phenyl-oxy-acrylic acids are isomeric with these (p. 557).

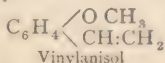
anhydride—coumarin. Its relations to common coumaric acid are perfectly similar to those of maleic to fumaric acid, and have not been further investigated. The basic salts of the acid, *e. g.*,  $C_6H_4(ONa).C_2H_2.CO_2Na$ , are obtained on boiling coumarin with alkalis, and differ from the salts of ordinary coumaric acid, which are prepared by strongly heating coumarin with alkalis (see above). From the former acids precipitate coumarin, from the latter, coumaric acid. If coumarin be boiled with KOH (2 molecules) and methyl iodide (2 molecules), in alcoholic solution, we obtain a dimethyl ether, which, on saponification, affords **Methylcoumarinic Acid**,  $C_6H_4(O.CH_3).C_2H_2.CO_2H$ , melting at  $90^\circ$ ; greater heat ( $150^\circ$ ) affords a dimethyl ether which, when saponified, yields **Methylcoumaric Acid**, melting at  $182^\circ$ . The latter acid is more readily obtained by boiling coumaric acid with KOH (1 molecule), methyl iodide and alcohol. It is, moreover, directly prepared from methyl salicylic aldehyde,  $C_6H_4(O.CH_3).CHO$  (p. 519), by means of sodium acetate, etc. Strong heat, boiling with hydrochloric acid, and even sunlight, converts methyl coumarinic acid into stable methyl coumaric acid. Sodium amalgam converts both acids into methyl-melilotic acid; and also yields the same addition product with bromine. Potassium permanganate oxidizes both to methyl salicylic acid. **Ethyl coumarinic** and **Ethyl coumaric Acid**,  $C_6H_4(O.C_2H_5).C_2H_2.CO_2H$ , manifest the same deportment; the former melting at  $102^\circ$ , the latter at  $133^\circ$  (*Ann.*, 216, 139).

**Coumarin**,  $C_9H_6O_2 = C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown C_2H_2 \end{smallmatrix} CO$ , the anhydride of coumarinic acid, occurs in *Asperula odorata*, in the Tonka beans (from *Dipterix odorata*), and in *Melilotus officinalis*. It is artificially prepared by heating salicylic aldehyde with sodium acetate and acetic anhydride. At first we get aceto-coumaric acid, which decomposes further into acetic acid and coumarin (p. 584). It is soluble in hot water, readily in alcohol and ether, crystallizes in shining prisms, possesses the odor of the *Asperula*, melts at  $67^\circ$ , and distils at  $290^\circ$ . When warmed it dissolves in alkalis with a yellow color; on boiling coumarinic and coumaric acids result (see above). Potassium permanganate destroys it (like the homologous phenols). Sodium amalgam changes it to melilotic acid (p. 554). Bromine converts it into a *dibromide*,  $C_9H_6Br_2O_2$ , melting at  $105^\circ$ .

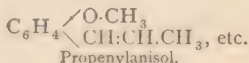
When salicylic aldehyde acts upon the higher fatty acids we derive homologous coumarins (p. 576). **Propionyl-coumarin**,  $C_{10}H_8O_2$ , from propionic acid, melts at  $90^\circ$ , and boils at  $292^\circ$ . **Butyryl-Coumarin**,  $C_{11}H_{10}O_2$ , from butyric acid, melts at  $71^\circ$ , and boils at  $299^\circ$ . The **ortho-butyryl-coumaric acid**,  $C_6H_4(OH).C_4H_6.CO_2H = C_{11}H_{12}O_3$ , melts at  $174^\circ$ .

The alkyl-ether acids,  $C_6H_4 \begin{smallmatrix} \diagup O.CH_3 \\ \diagdown CH:CH.CO_2H \end{smallmatrix}$ ,  $C_6H_4 \begin{smallmatrix} \diagup O.CH_3 \\ \diagdown CH:C(CH_3).CO_2H \end{smallmatrix}$ , etc.  
Methyloxyphenyl Acrylic Acid      Methyloxyphenyl Crotonic Acid.

derived from the alkyl-oxy-benzaldehydes (methyl salicylic aldehyde, methyl anisaldehyde), yield esters of unsaturated phenols (just as styrolene arises from cinnamic acid) by the action of HBr and a soda solution, when  $CO_2$  is eliminated, *e. g.* :—



and



The latter is the *anethol* found in anise oil.

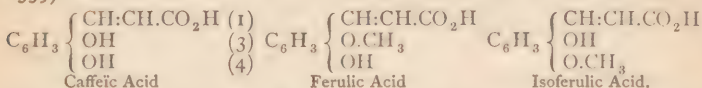


Alcoholic potassium hydroxide converts coumarin dibromide (see above) into **Coumarilic Acid**,  $C_9H_6O_3$ , melting at  $191^\circ$ , and not combining either with bromine or hydrobromic acid. On fusion with KOH it breaks up into salicylic and acetic acids, and when distilled with lime it yields  $CO_2$  and **Coumaron**,  $C_8H_6O$ , an oil boiling at  $169^\circ$ . Sodium amalgam converts it into **hydro-coumarilic acid**,  $C_9H_8O_3$ , melting at  $116^\circ$ . The constitution of these compounds is probably represented by the formulas (see *Ann.*, 216, 170):—

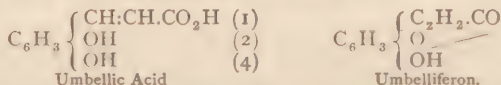


### Dioxyacids.

The dioxyphenyl acrylic acids are *caffeic acid* and its methyl ethers: *ferulic* and *isoferulic acids*, and *umbellic acid*, whose anhydride is *umbelliferon*. The first acids are intimately related to protocatechuic acid and its ethers, and to vanillic and iso-vanillic acids, since they have the side groups in the same position (p. 559):—



In *umbellic acid* the side-chains occupy the same position as in  $\beta$ -resorcylic acid (p. 558); one hydroxyl group is in the ortho-place referred to the side-chain containing carbon, hence the acid can yield an inner anhydride (*umbelliferon*), just as *ortho-coumaric acid* affords coumarin:—



**Caffeic Acid**,  $C_9H_8O_4$ , is obtained when the tannin of coffee (p. 564) is boiled with potassium hydroxide. It is prepared artificially from proto-catechuic aldehyde if the latter be heated with acetic anhydride and sodium acetate, and then the resulting diacetate saponified. It crystallizes in yellow prisms, and is very readily soluble in hot water and alcohol. The aqueous solution reduces silver solutions upon application of heat, but not alkaline cupric solutions. Ferric chloride causes a green coloration, which becomes dark red by the addition of soda. When fused with potassium hydroxide, caffeic acid decomposes into protocatechuic acid and acetic acid. Pyrocatechin results by its dry distillation. Sodium amalgam converts it into hydrocaffeic acid (p. 561).

**Ferulic Acid**,  $C_{10}H_{10}O_4$ , is the methyl-phenol ether of caffeic acid and corresponds to vanillin. It is found in *asafoetida*, from which it may be obtained by precipitation with lead acetate and by the subsequent decomposition of the lead salt. It has been synthetically prepared from vanillin when heated with sodium acetate, etc. It is very soluble in hot water, crystallizes in shining needles or prisms, and melts at  $169^\circ$ . When fused with potassium hydroxide, it affords protocatechuic acid and acetic acid. Potassium permanganate oxidizes the acetate to aceto-vanillin.

**Isoferulic Acid, Hesperetic Acid**,  $C_{10}H_{10}O_4$  (see above), was first obtained from the glucoside hesperidine, and is prepared by partially methylating caffeic acid (together with a little ferulic acid). It melts at  $228^\circ$ , and if fused with KOH decomposes into protocatechuic acid and acetic acid. The oxidation of its acetate produces isovanillic acid; sodium amalgam yields isohydroferulic acid (p. 561).

By the introduction of more methyl into ferulic and isoferulic acids, as well as caffeic acid, there results dimethyl caffeic acid,  $C_8H_8(O.CH_3)_2.C_2H_2.CO_2H$ , melting at  $181^\circ$ ; this is oxidized by potassium permanganate to dimethyl protocatechuic acid. *Methylene Caffeic Acid*,  $C_8H_8\left(\overset{O}{\text{C}}\text{CH}_2\right).C_2H_2.CO_2H$ , is obtained synthetically from piperonal (p. 521) by means of sodium acetate, etc.

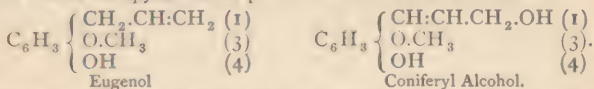
**Umbellic Acid**,  $C_9H_8O_4 = C_6H_3(OH)_2.C_2H_2.CO_2H$  (see above), is obtained by digesting umbelliferon with KOH, and then precipitating with acids. It is a yellow powder, decomposing about  $240^\circ$ . Its anhydride, corresponding to coumarin, is,

**Umbelliferon**,  $C_9H_6O_3$ , Oxycoumarin. It is found in the bark of *Daphne mezereum*, and is obtained by distilling different resins, such as galbanum and asafoetida. It is obtained synthetically from  $\beta$ -resorcylic aldehyde,  $C_6H_3(OH)_2.CHO$ , by means of sodium acetate, etc.; and also by the condensation of resorcinol with malic acid (p. 584). It affords fine needles, difficultly soluble in hot water and ether, melts at  $224^\circ$ , and sublimes undecomposed. When heated it has an odor resembling that of coumarin. It dissolves with a beautiful blue fluorescence, in concentrated sulphuric acid. It dissolves in cold alkaline hydroxides unaltered, but when heated umbellic acid is produced. Sodium amalgam converts it into hydro-umbellic acid (p. 561). Fusion with caustic alkali affords  $\beta$ -resorcylic acid and resorcinol.

When umbelliferon is treated with methyl iodide and caustic alkali it conducts itself like coumarin (p. 585). The products of the reaction are  $\alpha$ -Dimethyl-umbellic Acid, and the more stable  $\beta$ -Dimethyl-umbellic Acid,  $C_6H_3(O.CH_3)_2.C_2H_2.CO_2H$ ; these correspond to methyl coumarinic and methyl coumaric acids (*Ber.*, 16, 2115).

The so-called  $\beta$ -Methyl-umbelliferon,  $C_6H_3(OH)\overset{O}{\text{C}}(CH_3):CH\text{CO}$ , has been prepared synthetically by the condensation of resorcinol with aceto-acetic esters (p. 583). It melts at  $185^\circ$ , and when fused with KOH affords resacetophenone,  $C_6H_3(OH)_2.CO.CH_3$  (p. 523), and resorcinol (*Ber.*, 16, 2120).

Eugenol and coniferyl alcohol (p. 521) are closely related to ferulic acid. Their side chains occupy the same position as those in the latter:—

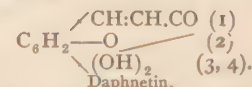
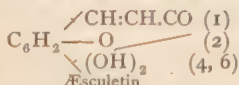


**Eugenol**,  $C_{10}H_{12}O_2$ , is found in oil of cloves (from the leaves of *Caryophyllus aromaticus*), in oil from the fruit of *Myrtus pimenta*, and in some other ethereal oils. Oil of cloves is a mixture of eugenol and turpentine oil; by shaking with an alcoholic potassium hydroxide solution it solidifies to a crystalline mass, potassium eugenate, which is pressed out, washed with alcohol, and decomposed by acids. Eugenol is an oil, with an aromatic odor, and boils at  $247^\circ$ . Ferric chloride gives a blue color to its alcoholic solution. All its properties are those of a phenol; acid chlorides replace one of its hydrogen atoms. Methyl iodide is set free when it is heated with hydriodic acid. Oxidation with potassium permanganate produces homovanillin, vanillin, and vanillic acid. If fused with potassium hydroxide it yields protocatechuic and acetic acids. Methyl iodide and KOH convert it into *methyl eugenate*,  $C_6H_3(O.CH_3)_2.C_3H_5$ , which yields dimethyl protocatechuic acid when oxidized with chromic acid. The side-chain,  $C_3H_5$ , in eugenol appears to possess the constitution of allyl,  $CH_2.CH:CH_2$  (*Ber.*, 15, 2069).

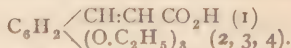
As a representative of the doubly unsaturated dioxyacid class we may mention

**Piperic Acid**,  $C_{12}H_{10}O_4 = C_6H_3 \begin{pmatrix} O \\ \diagup \diagdown \end{pmatrix} CH_2 \cdot CH:CH \cdot CH:CH \cdot CO_2H$ . Its side-chains are arranged like those in protocatechuic acid. The potassium salt is produced when the alkaloid piperine is boiled with alcoholic potassium hydroxide. It affords shining prisms. The free acid is almost insoluble in water, and crystallizes from alcohol in long needles, melting at  $217^\circ$ . Its salts with 1 equivalent of base are very difficultly soluble. It combines with four atoms of bromine. It is oxidized to piperonal when digested with potassium permanganate, and when fused with potassium hydroxide breaks up into acetic, oxalic and protocatechuic acids. Chromic acid destroys it completely. Sodium amalgam converts it into two isomeric **hydropiperic acids**,  $C_{12}H_{12}O_4$ ,  $\alpha$  and  $\beta$ . The  $\alpha$ -acid melts at  $78^\circ$ , and when digested with sodium hydroxide is converted into the  $\beta$ -acid, melting at  $131^\circ$ . The  $\alpha$ -acid yields a dibromide with bromine; the  $\beta$ -acid when acted upon with NaHg passes into the so-called **piperhydraonic acid**,  $C_{12}H_{14}O_4$ , melting at  $96^\circ$  (*Ann.*, **216**, 171).

*Æsculetin* and *Daphnetin* are anhydrides ( $\delta$ -lactones) of unsaturated trioxy-acids, and may also be designated dioxy-cumarins:—



The three hydroxyls in *æsculetin* have the same position as in phloroglucin,  $C_6H_3(OH)_3$  (1, 3, 5), and in *daphnetin* they are in the same relation as in pyrogallol. Their corresponding acids are only known as tri-ethyl-ether acids:—



**Æsculetin**,  $C_9H_6O_4$ , is present in the bark of the horse chestnut, partly free and partly as the glucoside *æsculin*, from which it is prepared by decomposition with acids or ferments. It crystallizes with a molecule of water in fine needles or leaflets, and dissolves with a yellow color in the alkalis. It reduces silver and alkaline copper solutions and receives a green color from ferric chloride.

Ethyl iodide and caustic alkali convert it (analogous to the deportment of umbelliferon and coumarin) into two isomeric **triethyl-æsculetinic acids** (see above), which are oxidized by  $MnO_4K$  into a *triethoxybenzoic acid*,  $C_6H_2(O.C_2H_5)_3 \cdot CO_2H$ , which parts with  $CO_2$  and becomes triethoxy-benzene,  $C_6H_3(O.C_2H_5)_3$ , and this yields phloroglucin,  $C_6H_3(OH)_3$ , upon fusion with  $KOH$  (*Ber.*, **16**, 2113).

**Daphnetin**,  $C_9H_6O_4$  (see above), is obtained by the decomposition of the glucoside *daphnin*. It is prepared synthetically by the condensation of pyrogallol with malic acid through the action of sulphuric acid (p. 584). It crystallizes in yellow needles or prisms, melting at  $255^\circ$ . It reduces silver and alkaline copper solutions, even in the cold, and receives a green color from ferric chloride. Ethyl iodide and caustic alkali convert it into **triethyl daphnetic acid**,  $C_6H_2(O.C_2H_5)_3 \cdot C_2H_2 \cdot CO_2H$ , from which we obtain Triethyl-pyrogallol-carboxylic Acid (p. 562)—*Ber.*, **17**, 1089—by means of  $MnO_4K$ .

Unsaturated *dibasic acids*. Under this head may be classed

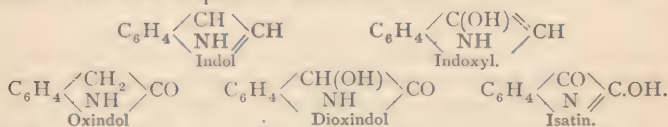
**Benzal-malonic Acid**,  $C_6H_5 \cdot CH:C(CO_2H)_2$ . This is produced in the condensation of benzaldehyde and malonic acid on digesting with glacial acetic acid (p. 512). It crystallizes from hot water in shining prisms, melting at  $196^\circ$ , with

decomposition into  $\text{CO}_2$ , and cinnamic acid. When it is boiled with water it splits into benzaldehyde and malonic acid; its salts, however, are stable.  $\text{NaHg}$  converts it into benzyl-malonic acid (p. 568). Bromine acting on its sodium salt produces  $\alpha$ -bromocinnamic acid. Its *diethyl ester*,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{C}(\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$ , is derived from benzaldehyde and malonic ester by means of  $\text{HCl}$  or  $\text{ZnCl}_2$ . It boils with slight decomposition about  $310^\circ$ . When saponified with aqueous sodium hydroxide benzal-malonic acid (*Ann.*, 218, 121) is the product.

The condensation of o-amidobenzaldehyde with malonic acid affords  $\beta$ -carbostyryl-carboxylic acid, a derivative of quinoline (*Ber.*, 17, 459).

## THE INDOL GROUP.

This embraces a series of bodies which can be regarded as derivatives of the simplest of them all—of *indol*,  $\text{C}_8\text{H}_7\text{N}$ . They were first derived from indigo-blue, and bear an intimate relation to the latter. The most important members are:—



The last three bodies, so far as concerns their synthetic methods of formation, are amido-anhydrides of ortho-amido-acids of benzene (p. 541). Oxindol is the lactam of o-amido-phenyl-acetic acid (p. 542), dioxindol the lactam of o-amido-mandelic acid (p. 553), while isatin represents the lactim of o-amido-benzoyl-formic acid (p. 546). On the other hand, these three bodies can be converted into each other, and have been obtained from isatin. By complete reduction they may be transformed into indol. All indol-derivatives contain a closed chain, comprising four carbon atoms (two of which belong to the benzene nucleus) and one nitrogen atom (p. 541) analogous to that in pyrrol, hence, indol may be called benzene-pyrrol. By the rupture of the pyrrol ring (in oxidations, etc.), the indol compounds are changed to ortho-amido-acids of benzene. Our knowledge of the indol derivatives and their kinship to indigo rests mainly upon the researches of Baeyer (*Ber.*, 13, 2254, 16, 2188).

**Indol**,  $\text{C}_8\text{H}_7\text{N}$ , was first obtained in the distillation of oxindol, and is a product of the reduction of indigo-blue with zinc dust. It is also produced by heating o-nitro-cinnamic acid with caustic potash and iron filings. From a theoretical standpoint, the following methods of formation are especially interesting: the reduction of o-nitrophenyl-acetaldehyde (p. 518) with zinc dust and ammonia, and the action of sodium alcoholate upon o-amido-chlorstyrolene (p. 573):—





This method represents indol as the anhydride of o-amidophenyl-vinyl alcohol,  $C_6H_4(NH_2).CH:CH(OH)$ .

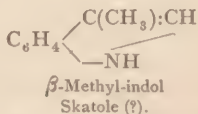
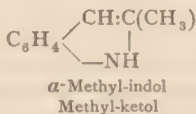
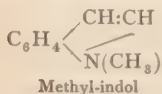
Indol may be obtained by various other methods; thus, by conducting the vapors of the mono- and di-alkyl anilines and ortho-toluidines through a tube heated to redness (*Ber.*, 10, 1262), or by distilling nitro-propenylbenzoic acid (p. 557) with lime; and in the pancreatic fermentation of albuminates, or (together with skatole) in the fusion of the latter with potassium hydroxide, but is best obtained by the first procedure (*Ber.*, 8, 336). Another noteworthy formation is that from the quinoline derivatives, *e. g.*, the fusion of carbostyryl with potassium hydroxide, or when tetrahydro-quinoline is conducted through a red-hot tube.

Indol crystallizes from water in shining leaflets, melting at  $52^\circ$  and boiling about  $245^\circ$  with partial decomposition. It is readily volatilized in aqueous vapor. Its vapor density (under diminished pressure) corresponds to the formula  $C_8H_7N$ . It possesses a peculiar odor, resembling that of naphthylamine. A pine splinter moistened with hydrochloric acid and dipped into its alcoholic solution acquires a cherry-red color. If some fuming nitric acid (or  $NaNO_2 + H_2SO_4$ ) be added to the aqueous solution, it becomes red and then separates a red nitrate of so-called *nitroso-indol* (of complex constitution). Indol possesses but very feeble basic properties, and is scarcely dissolved by dilute hydrochloric acid. Water decomposes its salts. It combines with benzene, yielding a derivative, which affords red needles when crystallized from benzene. Ozone conducted through water containing suspended indol causes a gradual precipitation of indigo-blue.

**Acet-indol**,  $C_6H_4 \begin{smallmatrix} < CH:CH \\ N(C_2H_5O) \end{smallmatrix} >$ , is obtained when indol is heated to  $180^\circ$  with acetic anhydride. It melts at  $183^\circ$ . Oxindol digested with  $PCl_5$  and  $POCl_3$  yields *dichlor-indol*,  $C_6H_4 \begin{smallmatrix} < CCl:CCl \\ HN \end{smallmatrix} >$  (shining leaflets, melting at  $104^\circ$ ). The latter is converted by methyl iodide and sodium alcoholate into *methyl-dichlor-indol*,  $C_6H_4 \begin{smallmatrix} < CCl:CCl \\ N(CH_3) \end{smallmatrix} >$  (*Ber.*, 15, 786).

**Iso-indol**,  $C_{16}H_{14}N_2$  (p. 523), and **di-indol**,  $C_{16}H_{14}N_2$ , or **indolin** are polymeric forms of indol. We obtain the second by heating indigo-white with baryta water and zinc dust. It sublimes in yellow needles, melting at  $140^\circ$ .

*Alkyl Indols:—*



**Methyl-Indol**,  $C_8H_6N(CH_3)$ , has been obtained from the condensation product of phenyl-methyl-hydrazine (p. 473) with pyrrocemic acid. The first product of the reaction is **Methyl-indol-carboxylic acid**, which splits into  $CO_2$  and methyl-indol (*Ber.*, 17, 559). It is an oil, boiling at  $239^\circ$ , and in its reaction resembles indol. Oxidation converts it into methyl pseudo-isatin. **Ethyl Indol**,  $C_8H_6N.C_2H_5$  (boiling near  $247^\circ$ ), is prepared the same as the preceding compound, and yields ethyl pseudo-isatin (p. 524).

$\alpha$ -Methyl-Indol,  $C_8H_7(CH_3)NH$ , Methyl-Ketol, arises in the anhydride-formation of ortho-amido-benzyl methyl ketone (p. 524). It crystallizes in thin leaflets, melts at  $50^\circ$ , has an odor like that of indol, and manifests perfectly similar reactions. Oxidation with  $MnO_4K$  (by rupture of the pyrrol ring at the point of the double binding) converts it into aceto-ortho amido-benzoic acid,



Skatole,  $\beta$ -Methyl-indol,  $C_8H_7(CH_3)NH$  (?), occurs in human faeces (with a little indol). It may be obtained, together with indol, from reduced indigo (p. 590), by the putrefaction of albuminoids, or (with indol) in the fusion of the same with potassium hydroxide. In the putrefaction skatole carboxylic acid,  $C_9H_8N.CO_2H$ , first results; this melts at  $161^\circ$ , and decomposes into  $CO_2$  and skatole. It is synthesized on heating glycerol with aniline- $ZnCl_2$ , or by the distillation of nitrocumic acid (p. 545) with zinc dust or iron filings (*Ber.*, 16, 710, 2927). It crystallizes in leaflets, melting at  $94^\circ$ , and in a perfectly pure condition has a penetrating (not fecal) odor.

Oxindol,  $C_8H_7NO = C_6H_4 \begin{array}{c} \diagup CH_2 \\ \diagdown NH \end{array} > CO$ , the lactam of ortho-amido phenyl acetic acid (p. 589), was first obtained by the reduction of dioxindol with tin and hydrochloric acid, or with  $NaHg$  in acid solution. It is also produced in the reduction of aceto-o amido-mandelic acid (p. 554) with hydriodic acid. It crystallizes from hot water in colorless needles, and melts at  $120^\circ$ . It oxidizes to dioxindol when exposed in a moist condition; by protracted boiling it will reduce an ammoniacal silver solution. It has both basic and weak acid properties, forms a stable hydrochloride, and dissolves in alkalis. If heated to  $150^\circ$  with baryta water it is converted into o-amido-phenyl-acetic acid (p. 589).

Oxindol boiled with acetic anhydride yields Aceto-oxindol,  $C_6H_4 \begin{array}{c} \diagup CH_2.CO \\ \diagdown N.CO.CH_3 \end{array}$ ,

which crystallizes in long needles, and melts at  $126^\circ$ . It dissolves to aceto-ortho-amido-phenyl acetic acid in sodium hydroxide (p. 542). The action of nitrous acid upon the aqueous solution of oxindol causes a transposition and isatoxim results (p. 596); this was formerly taken for nitroso-oxindol; the latter passes, by reduction with tin and hydrochloric acid, into the so-called Amido-

oxindol,  $C_6H_4 \begin{array}{c} \diagup CH(NH_2) \\ \diagdown CO \end{array} > CO$  (?). Ferric chloride oxidizes this to isatin.

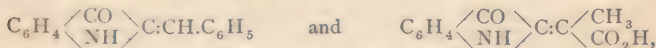
An isomeride of the last compound is  $H_2N.C_6H_3 \begin{array}{c} \diagup CH_2 \\ \diagdown NH \end{array} > CO$ , p-Amido-oxindol, which is produced by the reduction of dinitrophenyl acetic acid (p. 540). Isatoxim also results from it when it is acted upon by nitrous acid and boiled with alcohol (*Ber.*, 16, 518).

Ethyl Oxindol,  $C_6H_4 \begin{array}{c} \diagup CH_2.CO \\ \diagdown N(C_2H_5) \end{array} >$ , is obtained on boiling oxindol with sodium ethylate (1 equivalent) and ethyl iodide. It is an oil, volatile with aqueous vapor. If it be heated with baryta water or with concentrated hydrochloric acid to  $150^\circ$  the ethyl group will not be split off (compare p. 541) (*Ber.*, 16, 1705).



**Pseudo-indoxyl** (see above) is known only in its derivatives. Its isonitroso-compound,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NH \end{smallmatrix} C(N.OH)$ , formerly considered nitroso-indoxyl, is produced by the action of nitrous acid upon ethoxyindoxyl acid. A transposition occurs here. It is identical with pseudo-isatxim (p. 596).

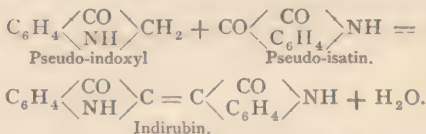
The derivatives of pseudo-indoxyl



are similarly obtained from indoxyl or indoxyl acid by condensation with benzaldehyde and pyrrocemic acid. They are called the indogenides of the latter compounds, and are perfectly similar to *pseudo-isatin ethoxim* (p. 596). The divalent group,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NH \end{smallmatrix} C$ , is termed *indogen* (*Ber.*, 16, 2197).

The condensation of isatin with benzenes affords perfectly analogous indogenides. In this case the isatin changes to pseudo-isatin,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NH \end{smallmatrix} CO$ .

**Indirubin**,  $C_{16}H_{10}N_2O_2$ , is of this class. It is isomeric with indigo-blue, and appears in nearly all the indigo syntheses, and in its entire character is very similar to this substance. It is produced by effecting the condensation of indoxyl (pseudo-indoxyl) with isatin (pseudo-isatin) by means of a dilute soda solution (*Ber.*, 17, 976), and therefore, may be called an indogenide of pseudo-isatin:—



In the same manner indoxyl may be oxidized (by the union of two pseudo-indoxyl groups with separation of water) to indigo-blue, which, therefore, is to be considered a *di-indogen* (*Ber.*, 16, 2204).

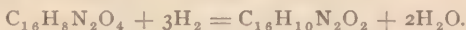
**Indoxanthic Ester**,  $C_{11}H_{11}NO_4 = C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NH \end{smallmatrix} C(OH).CO_2R$ , results from the oxidation of indoxyl ester with ferric chloride or chromic acid. It yields a nitrosamine with nitrous acid (*Ber.*, 15, 774). Further oxidation produces anthranil oxalylic ester,  $C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown NH.CO.CO_2R \end{smallmatrix}$  (p. 536)—this is analogous to the formation of aceto-anthranilic acid (p. 536) from methyl ketol. Indoxanthic ester reverts to indoxyl ester when reduced.

**Isatogenic Ester**,  $C_{11}H_9NO_4 = C_6H_4 \begin{smallmatrix} \diagup CO.C.CO_2.C_2H_5 \\ \diagdown N \end{smallmatrix} O$  (?), is obtained by a transposition of the isomeric o-nitrophenyl propiolic ester when it dissolves in concentrated sulphuric acid (p. 582). It crystallizes in yellow needles, melting at 115°. Various reducing agents convert it into indoxyl ester, but with ferrous sulphate we get indoxanthic ester. In the solution of free o-nitrophenyl acetic acid in sulphuric acid, the free **Isatogenic Acid**,  $C_8H_4NO_2.CO_2H$ , is very probably produced; it cannot, however, be isolated. Isatin,  $C_8H_5NO_2$ , exists in the solution diluted with water.

**Di-isatogen**,  $C_{16}H_8N_2O_4$ , isomeric with the preceding, is similarly formed by dissolving o-dinitrodiphenyl-diacetylene (p. 574) in sulphuric acid (by the union



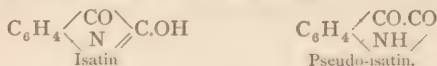
of two isatogen groups,  $C_6H_4 \cdot C_2NO_2$ ). It crystallizes in red needles and by reduction yields *indigo blue* :—



On adding sulphate of iron to the solution of isatogenic ester, di-isatogen or o-nitrophenyl propiolic acid in sulphuric acid, the solution becomes blue in color and *Indoin*,  $C_{32}H_{20}N_4O_5$  (?), separates. This is very similar to indigo-blue. It is also formed by adding o-nitrophenyl propiolic acid to the solution of indoxyl or indoxyllic acid in sulphuric acid.

**Di-oxindol**,  $C_8H_7NO_2 = C_6H_4 \begin{smallmatrix} \diagup CH(OH) \\ \diagdown NH \end{smallmatrix} CO$ , is the lactam of o-amido-mandelic acid, not capable of existing in a free condition, or hydrindic acid (p. 589). It is more readily obtained by boiling isatin with zinc dust, water and a slight quantity of hydrochloric acid. It is rather easily soluble in water and alcohol, crystallizes in colorless prisms, melting at  $180^\circ$  and decomposing about  $195^\circ$  with formation of aniline. It oxidizes readily in aqueous solution to *isatid* and *isatin*. It forms salts with bases and acids; it combines with two equivalents of the former. Nitrous acid converts it into the nitroso-compound,  $C_8H_6(NO)NO_2$ , melting at  $300^\circ$  and subliming in white needles. Di-oxindol heated with acetic anhydride to  $140^\circ$  yields *aceto-oxindol*  $C_6H_4 \begin{smallmatrix} \diagup CO.CO \\ \diagdown N(CO.CH_3) \end{smallmatrix}$ , melting at  $127^\circ$  and dissolving in baryta water with the formation of aceto-o-amido-mandelic acid (p. 554).

**Isatin**,  $C_8H_5NO_2$ , is the lactim of o-amido-phenyl-glyoxylic acid or *isatinic acid* (p. 546), whose lactam, the hypothetical *pseudo-isatin*, is known only in its derivatives :—



Isatin was first obtained by the oxidation of indigo. It is also prepared from oxindol by transposition into the so-called amido-oxindol (p. 591) and then oxidizing the latter with ferric chloride. It arises in a similar manner from indoxyl. Its ready formation from o-nitro-phenyl-propionic acid by boiling with alkalis (p. 581) and by the decomposition of isatogenic acid (p. 593), is worthy of remark. It is also obtained from  $\alpha$ -oxyquinoline (carbostyryl) in its oxidation with potassium permanganate.

The easiest method of preparing isatin consists in oxidizing indigo with nitric acid (*Ber.*, 17, 976). To purify it, dissolve it in potassium hydroxide, add hydrochloric acid as long as a black precipitate is formed, and then treat the filtrate with hydrochloric acid.

Isatin crystallizes in yellowish-red monoclinic prisms, melting at  $201^\circ$ , and subliming partially undecomposed. It dissolves in water and alcohol with a reddish-brown color. It dissolves in caustic alkalis (equivalent quantities), forming salts, *e. g.*,  $C_8H_4NKO_2$ . The

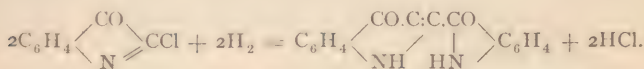
solution, violet at first, soon becomes yellow. with the production of isatinates; digestion with excess of alkali causes the immediate transformation. Acids liberate the readily soluble isatinic acid from the salts; and on standing, more quickly upon the application of heat, this changes to isatin, at the same time assuming a yellowish-red color. Isatin also possesses a ketone-like character; it unites with alkaline bisulphites to crystalline compounds, with hydroxylamine to isatoxim (p. 596), and with phenyl-hydrazine hydrochloride to a yellow compound, melting at  $210^{\circ}$ , which may be employed in detecting isatin (*Ber.*, 17, 577). It affords a dark blue solution with benzene containing thiophene and sulphuric acid (p. 398). Water precipitates *indophenin*, a body containing sulphur, from this solution.

Isatin yields nitrosalicylic acid when oxidized with nitric acid, and aniline when fused with potassium hydroxide. When reduced (boiling with zinc dust, etc), it first becomes dioxindol,  $C_8H_7NO_2$ ; with ammonium sulphide we get an intermediate product—*isatid*,  $C_{16}H_{12}N_2O_4$ . This is a colorless powder, readily re-oxidizing to isatin.

In a solution of potassium-isatin, or in one of ammonia containing isatin, silver nitrate precipitates *silver isatin*,  $C_8H_4AgNO_2$ , a red compound. Chlorine and bromine (in glacial acetic acid) convert isatin into substitution products, which conduct themselves just like isatin, and if dissolved in alkalis yield substituted isatinic acids. Nitration in the cold produces *nitroisatin*,  $C_8H_4(NO_2)NO_2$ —red needles, melting about  $230^{\circ}$ .

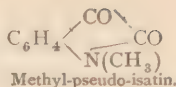
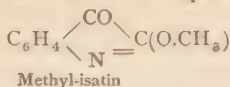
If  $NH_3$  should act upon isatin suspended in ether, there will result *Imesatin*,  $C_8H_5NO(NH)$ , forming dark yellow crystals, and when digested with alkalis or acids, decomposing again into isatin and  $NH_3$ . An analogous compound is *Tolyl-methylimesatin*,  $C_8H_4(CH_3)NO(N.C_7H_7)$ , in which we have the residue of para-toluidin,  $C_6H_4(CH_3)N-$ , in place of the  $NH$ -group. It is obtained by heating p-toluidine with dichloroacetic acid (by condensation) (*Ber.*, 16, 2261). Concentrated hydrochloric acid decomposes it (like imesatin) into toluidine and p-*Methylisatin*,  $C_8H_4(CH_3)NO_2 = C_6H_3(CH_3):C_2NO_2H$ . The latter resembles isatin; with  $PCl_5$  it affords p-*Methylisatin chloride*,  $C_8H_4(CH_3)NOCl$ , which (in the same manner as isatin chloride, etc.) may be converted into *dimethyl indigo-blue*,  $C_{16}H_8(CH_3)_2N_2O_2$  (methylated in the benzene nucleus.)

**Isatin Chloride**,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown N \end{smallmatrix} \diagup CCl$ , is produced by digesting isatin with  $PCl_5$  (in benzene solution). It crystallizes in brown needles and dissolves with a blue color in ether, alcohol and glacial acetic acid. Hydriodic acid or zinc dust acting on its glacial acetic acid solution produces *indigo-blue* :—



We can also obtain from the substituted isatin (brom-, nitro-, methyl-isatin) substitution products of indigo blue, dibrom-, di-nitro-, and dimethyl-indigo blue (*Ber.*, 12, 456).

Ether derivatives of isatin and pseudo-isatin :—

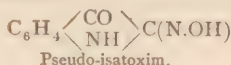


The *alkyl isatins* result from the action of alkyl iodides upon silver-isatin, and are blood-red colored crystalline bodies. **Methyl-isatin**,  $\text{C}_8\text{H}_4\text{NO}_2(\text{CH}_3)$ , melts at  $102^\circ$ . **Ethyl dibrom-isatin**,  $\text{C}_8\text{H}_2\text{Br}_2\text{NO}_2(\text{C}_2\text{H}_5)$ , at  $88^\circ$ . They are saponified by alkalies, and yield salts of isatin and isatinic acid. Acids separate isatin from these. Ammonium sulphide with air contact converts them at once into indigo blue (*Ber.*, 15, 2093).

When isatin is boiled with acetic anhydride a transposition occurs and we obtain **Aceto-pseudo-isatin**,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO}.\text{CO} \diagdown \\ \diagdown \text{N}(\text{CO}.\text{CH}_3) \end{array}$ , crystallizing in yellow needles, and melting at  $141^\circ$ . When digested with water or acids it splits into acetic acid and isatin. It dissolves in alkalies, forming salts of aceto-isatinic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO}.\text{CO}_2\text{H} \\ \diagdown \text{NH}(\text{CO}.\text{CH}_3) \end{array}$  (p. 546), which decompose on warming into isatinates and acetic acid.

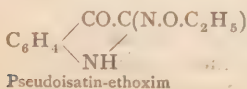
**Ethylpseudoisatin** (see above) is obtained by the reduction and subsequent oxidation of ethoxypseudo-isatin-ethoxim (p. 597). It crystallizes in large, blood-red crystals, melting at  $95^\circ$ . It dissolves immediately in alkalies with a yellow color, forming salts of ethyl isatinic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO}.\text{CO}_2\text{H} \\ \diagdown \text{NH}.\text{C}_2\text{H}_5 \end{array}$ , from which acids at once separate ethylpseudo-isatin (*Ber.*, 16, 2193). The latter is also obtained from ethyl indol (p. 590), by oxidation with a hypobromite (*Ber.*, 17, 559). **Methyl-pseudoisatin**, formed in the same way, consists of red needles, melting at  $134^\circ$ .

#### Isonitroso-derivatives of Isatin and Pseudoisatin.

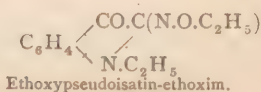


**Isatoxim**,  $\text{C}_8\text{H}_6\text{N}_2\text{O}_2$ , was first obtained by the action of nitrous acid upon oxindol (p. 591), and was, therefore, formerly considered nitroso-oxindol. It is also prepared (analogous to the formation of the acetoxims, p. 161), from isatin and hydroxylamine; or from para-amido-oxindol (p. 591), by action of nitrous acid, and boiling with alcohol (*Ber.*, 16, 518). It crystallizes from alcohol in yellow needles, and melts at  $202^\circ$ , with decomposition. It dissolves with a yellow color in the alkalies. When reduced with tin and hydrochloric acid it yields so-called amido-oxindol (p. 591). By the successive action of ethyl iodide upon the silver salt we obtain a mono-, and a diethyl derivative from which isatin (*Ber.*, 16, 1706) is formed by reduction and subsequent oxidation.

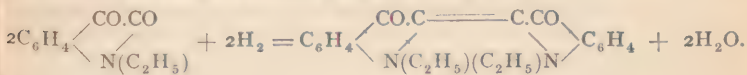
**Pseudo-isatoxim** (see above) is prepared (by transposition) by the action of nitrous acid upon ethyl indoxyl acid. It was formerly considered nitroso-indoxyl (p. 593). It crystallizes from alcohol in shining yellow needles, and decomposes at about  $200^\circ$ . It does not give the nitroso reaction. It dissolves in alkalies and is separated again by  $\text{CO}_2$  (*Ber.*, 15, 782). Ethyl iodide and sodium ethylate convert it into :—



and



The first yields isatin by reduction and oxidation (as does isatoxim and its two ethers, loc. cit.). The same treatment applied to ethoxy-pseudo-isatin-ethoxim yields ethylpseudoisatin,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO.CO} \\ \diagdown \quad \diagup \\ \text{N}(\text{C}_2\text{H}_5) \end{smallmatrix}$  (see above). The reduction of ethylpseudo-isatin-ethoxim with ammonium sulphide produces diethyl indigo, in which the two ethyl groups are united to nitrogen (*Ber.*, 16, 2201):—

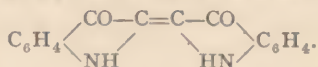


**Anthroxan Aldehyde**,  $\text{C}_8\text{H}_5\text{NO}_2 = \text{C}_6\text{H}_4 \begin{smallmatrix} \text{C} & \text{---} & \text{CHO} \\ | & & | \\ \text{N} & & \text{O} \end{smallmatrix}$  (with an atomic grouping similar to that of isatogenic ester), is isomeric with isatin, and is formed when ortho-nitrophenyl oxyacrylic acid (p. 557) is boiled with water (together with anthranil) (*Ber.*, 16, 2226). Silver oxide converts it into **anthroxanic acid**,  $\text{C}_7\text{H}_4\text{NO.CO}_2\text{H}$ .

## INDIGO-BLUE.

**Indigo-blue or Indigotin.** This commercially important chromogen is found in ordinary indigo and possesses the molecular formula,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ , which is in accord with its vapor density. The innumerable synthetic methods for its production, already mentioned, were discovered by A. Baeyer. The most important of these are: the reduction of isatin chloride (p. 595) first with phosphorus (1870), then with zinc dust or HI (1879); the transformation of ortho-nitrophenyl propiolic acid (p. 581) by digestion with alkalis and reducing agents (1880); the condensation of ortho-nitrobenzaldehyde with acetone in alkaline solution (pp. 515 and 575), acetaldehyde and pyroracemic acid (p. 583) (1882); and the conversion of  $\alpha$ -dibrom-ortho-nitro-acetophenone (p. 523) by boiling with alkalis (1882) (*Ber.*, 17, 963).

According to A. Baeyer's investigations the constitution of indigo blue is very probably expressed by the formula:—



This accounts best for its entire deportment and all its transformations.

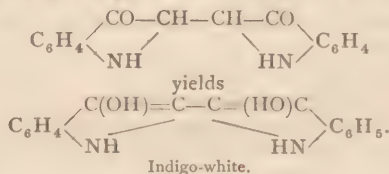
According to this formula indigo-blue contains two indol groups,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C} & \text{---} & \text{C} \\ \diagdown & & \diagup \\ \text{N} & & \end{smallmatrix}$ , in combination with each other. That the union is through the carbon atoms follows from the synthesis of indigo-blue from ortho-dinitro-diphenyl-diacetylene (p. 574) and, therefore, diphenyl-diacetylene,  $\text{C}_6\text{H}_5\text{.C} \text{ : } \text{C} \text{ : } \text{C}_6\text{H}_5$ , may be looked upon as the parent hydrocarbon of indigo-blue. This we infer also from the formation of indigo-blue from the indoxyl and isatogenic derivatives, which is



analogous to that of the indogenides (p. 593). As arguments for the existence of the group,  $C_6H_4 \begin{smallmatrix} \diagup CO.C \\ \diagdown N \end{smallmatrix}$ , we have the production of indigo-blue from isatin chloride and the isatin ethers (p. 595), as well as from brom-acetophenones (see above); from the indoxyl compounds, from indoxanthic ester and di isatogen (p. 593). Another support for this view is the fact that only those derivatives of ortho-nitro-cinnamic acid,  $C_6H_4(NO_2).CH:CH.CO_2H$ , yield indigo in which the carbon atom joined to the benzene nucleus is also in connection with hydroxyl or oxygen; thus the ortho-nitro-phenyl-oxyacrylic acids (p. 557) and not the ortho-nitro-cinnamic acid afford indigo. The condensation products of ortho-nitrobenzaldehyde behave similarly; ortho-nitrophenyl-lactic methyl ketone,  $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$ , yields indigo, but ortho-nitro-cinnamyl-methyl ketone (p. 575) does not. With the latter bodies (in the formation of indigo blue) there occurs a splitting-off of the excessive carbon atoms of the side-chains in the form of formic acid, acetic acid, etc.

Finally, the presence of 2 NH groups in indigo-blue is rendered very probable by the formation of di-ethyl indigo from ethyl pseudo-isatoxim (p. 596).

In the production of indigo-blue from indoxyl derivatives there occurs, in all probability, a conversion of indoxyl into pseudo-indoxyl and pseudo-isatin, and this leads us to regard indigo-blue as a *di-indogen*, corresponding to the indogenides of benzaldehyde, etc. (p. 593). The absorption of two hydrogen atoms reduces indigo-blue to *indigo-white*,  $C_{16}H_{12}N_2O_2$ , which has the character of a phenol. In this reaction the doubly united carbon atoms are at first saturated and then the indogen group is changed to the indoxyl group:—



Indigo-blue constitutes the principal ingredient of commercial **Indigo**, derived from different *Indigoferæ* and from woad (*Isatis tinctoria*). It occurs in these plants as a glucoside, called *indican*, which parts with its variety of glucose and becomes indigo-blue, when boiled with dilute acids, or if acted upon with a ferment (if the various portions of the plant be covered with water and exposed to the action of the air). The indigo-blue separates in the form of a powder.

Commercial indigo is a mixture of several substances, of which the indigo-blue is alone valuable. Boiling acetic acid extracts *indigo gluten* from it; and dilute potassium hydroxide takes out *indigo brown*, which is precipitated as a brown mass by sulphuric acid. The residue finally yields to boiling alcohol the *indigo-red*, a red powder which dissolves in alcohol and ether with this color. The residual mass is almost pure indigo-blue.

Indigo-blue can be obtained from commercial indigo by sublimation, but it nearly all decomposes by the operation. It is advisable to first reduce indigo to soluble indigo-white, which can

then be oxidized to indigo-blue by the exposure of the alkaline solution to the air.

Grape sugar is the best reducing agent for indigo. The latter, in a finely divided state, is mixed with an equal weight of grape sugar, and upon this are poured  $1\frac{1}{2}$  parts concentrated NaOH and hot alcohol or water (150 parts), and the whole allowed to stand in a closed flask filled with the same liquid for some hours. The clear yellow solution is next poured into dilute hydrochloric acid and shaken with air (*Ann.*, 195, 305).

Indigo-blue or indigotin is a dark-blue powder with a reddish glimmer; it becomes metallic and copper-like under pressure. It sublimes in copper-red, metallic, shining prisms. It is insoluble in water, alcohol and ether, in alkalis and dilute acids, and is odorless and tasteless. It dissolves in hot aniline with a blue, in molten paraffin with a purple-red color, and can be crystallized from these solvents. It crystallizes from hot oil of turpentine in beautiful blue plates. At  $300^{\circ}$  it is converted into a dark-red vapor. If boiled with potassium hydroxide and manganese peroxide, it yields anthranilic acid (p. 536); aniline results on distilling with potassium hydroxide.

We will yet mention some of the substituted indigotins, which are quite similar to indigotin and have been prepared synthetically.

Dichlor, brom-, nitro-indigos result from the substituted isatins (p. 596), and from brom o-nitroacetophenones (p. 597). Tetrabrom-indigo is obtained from o-nitro-dichlor-benzaldehyde by condensation with acetone (p. 515). Dimethyl indigos result from nitro-m-toluic aldehyde (p. 517) and p-methyl-isatin (p. 595). Diethyl indigo (its imid-groups contain ethyl) is obtained from ethyl-pseudo-isatin-ethoxim (p. 596).

The isomerides of indigotin are indigo-red, present in commercial indigo, indirubin, the indogenide of pseudoisatin (p. 594), indigo-purpurin, formed together with indigotin from isatin chloride (p. 594) and indin. The latter is obtained by the action of alcoholic potassium hydroxide upon isatid (p. 594), or by boiling dioxindol with glycerol. Di-isatogen,  $C_{16}H_8N_2O_4$ , and indoïn (p. 594) bear a close relation to indigotin.

Indigo White,  $C_{16}H_{12}N_2O_2$ , is obtained by the reduction of indigo-blue (see above). It can be precipitated from its alkaline solution by hydrochloric acid (air being excluded) as a white crystalline powder, soluble in alcohol, ether and the alkalis, with a yellowish color. It rapidly re-oxidizes to indigo-blue by exposure to the air. It yields di-indol when heated with baryta-water and zinc dust.

When indigo-blue is dissolved in concentrated sulphuric acid (8-15 parts) and digested for some time, we get *indigotin monosulphonic acid*,  $C_{16}H_9N_2O_2 \cdot SO_3H$  (phœnicin sulphuric acid), and *indigotin disulphonic acid*,  $C_{16}H_8N_2O_2 \cdot (SO_3H)_2$  (œcerulin sulphuric acid). Water precipitates the former from its solution as a blue powder, soluble in pure water and alcohol, but not in dilute acids. Its salts with the bases possess a purple-red color and dissolve with a blue color in water.

The disulphonic acid is obtained when indigo is digested with strongly fuming

sulphuric acid. It can be absorbed from its aqueous solution by clean wool and again removed from the latter by ammonium carbonate. Its alkali salts, *e. g.*  $C_{16}H_8N_2O_2(SO_3K)_2$ , are difficultly soluble in salt solutions, and are thrown out from their solution in the form of dark-blue precipitates by alkaline carbonates and acetates. They constitute in commerce what is known as *indigo-carmine*. When the indigotin sulphonic acids are reduced, they yield, just as does indigo-blue, the indigo-white sulphonic acids.

Goods (wool) are dyed in two ways with indigo: the wool is immersed in the aqueous solution of indigotin sulphonic acid (Saxony-blue dyeing), or the indigo-blue is changed by fermentation to indigo-white (indigo-vat), the weaving saturated with the latter and exposed to the air, when indigo-blue forms and sets itself upon the fibre. In printing, a mixture of ortho-nitrophenyl propiolic acid and an alkaline reducing agent (potassium xanthate, etc.) are sometimes substituted for the indigo. Steaming causes the formation of indigo-blue.

## DERIVATIVES WITH TWO OR MORE BENZENE NUCLEI.

Although in general very stable the benzenes yet possess to a high degree the power, by exit of hydrogen, of combining with each other in part directly, and partly by the assistance of other carbon atoms. The hydrocarbons derived in this manner afford numerous derivatives.

They may be classified as follows: (1) those with directly combined benzene nuclei; (2) those in which the benzene nuclei are joined by 1 carbon atom; (3) those with benzene nuclei linked together by two or more carbon atoms; (4) those with condensed benzene nuclei.

### 1. Derivatives of directly combined benzene nuclei.

#### DIPHENYL GROUP.\*

**Diphenyl**,  $C_{12}H_{10} = C_6H_5.C_6H_5$ , results from the action of sodium upon the solution of brom-benzene in ether or benzene:  $2C_6H_5Br + Na_2 = C_{12}H_{10} + 2NaBr$ . It is best obtained by conducting benzene vapors through iron tubes heated to redness. The tubes are filled with pieces of pumice stone. The yield of diphenyl (*Ber.*, 9, 547, and 10, 1602), is about 50 per cent. of the benzene taken. Diphenyl is also produced in slight amount when benzoic acid is distilled with lime or if potassium phenoxide be distilled with potassium benzoate. It is present in that portion of coal-tar which boils about  $240-260^\circ$ .

Diphenyl crystallizes from alcohol and ether in large, colorless leaflets, melting at  $70.5^\circ$ , and boiling at  $254^\circ$ . If dissolved in glacial acetic acid and oxidized with chromic anhydride it yields benzoic acid.

\* Consult *Ann.*, 207, 363, for a tabulation of these diphenyl derivatives.

The halogens, nitric acid and sulphuric acid convert diphenyl into mono- and di-substitution products. In the first, *e. g.*,  $C_{12}H_9Br$ ,  $C_{12}H_9(NO_2)$ ,  $C_{12}H_9SO_3H$ , the substitution groups occupy the para-position, referred to the point of union of the two benzene nuclei. When these are oxidized with nitric acid we obtain para-derivatives of benzoic acid, the other benzene nucleus being destroyed. The di-derivatives *e. g.*,  $C_{12}H_8Br_2$ , occur in two isomeric modifications. The di-para-derivatives predominate; in these the two side-chains have the para-position referred to the point of union. Chromic acid oxidizes them to two para-derivatives of benzoic acid; thus from brom-nitro-diphenyl we get para-brom- and para-nitro-benzoic acid.

The energetic chlorination of diphenyl and its derivatives (p. 421), produces *perchlor-diphenyl*,  $C_{12}Cl_{10}$ ; brilliant plates or prisms, melting above  $280^\circ$ , and boiling at about  $440^\circ$ . Like perchlor-benzene, it is very stable, and does not undergo any further decomposition.

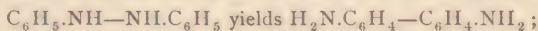
The nitration of diphenyl in the cold, or when dissolved in glacial acetic acid, yields two nitro-diphenyls,  $C_{12}H_9(NO_2)$ ; the para-compound is not soluble in alcohol, melts at  $113^\circ$ , boils at  $340^\circ$ , and when oxidized with chromic acid becomes para-nitro-benzoic acid. The other nitro-diphenyl (very probably ortho) affords plates, melting at  $37^\circ$ .

Fuming nitric acid produces  $\alpha$ - and  $\beta$ -dinitro-diphenyl,  $C_{12}H_8(NO_2)_2$ ; the former (di-para) is very difficultly soluble in hot alcohol, and melts at  $230^\circ$ , the latter melts at  $93.5^\circ$ .

Amido-derivatives result from the nitro- by reduction with tin and hydrochloric acid.

**Amido-diphenyl**,  $C_{12}H_9(NH_2)$ , xenylamine, crystallizes from hot water or alcohol in colorless needles, melting at  $49^\circ$  and boiling at  $322^\circ$ .

**Diamido-diphenyl**,  $C_{12}H_8(NH_2)_2$ , (di-para), **Benzidine**, is obtained: by the reduction of  $\alpha$ -dinitrodiphenyl; by the action of sodium upon para-brom-aniline; by the molecular transposition of hydrazobenzene on standing in contact with acids (p. 468):—



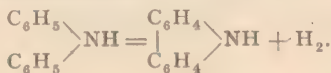
also by heating azobenzene with fuming hydrochloric acid to  $150^\circ$ , and on conducting sulphur dioxide into its alcoholic solution, when very probably hydrazobenzene is first produced.

Benzidine dissolves easily in hot water and alcohol, crystallizes in silvery leaflets melting at  $188^\circ$ , and subliming with partial decomposition. It affords salts with two equivalents of acid; the sulphate,



is insoluble in water. It oxidizes to quinone if boiled with  $MnO_2$  and dilute sulphuric acid.

An isomeric *diamido-diphenyl* (**Diphenylin**) is obtained from  $\beta$ -dinitrodiphenyl and (together with benzidine) by the reduction of azobenzene with tin and hydrochloric acid. It crystallizes in needles, melting at  $45^\circ$ . **Carbazol**, imido-diphenyl,  $C_{12}H_9N$ , is obtained by conducting the vapors of diphenylamine or aniline through a highly heated tube:—





It occurs in that portion of crude anthracene boiling at  $320-360^{\circ}$ , and is a by-product in the manufacture of aniline. Carbazol dissolves in hot alcohol, ether and benzene, crystallizes in colorless leaflets, melts at  $238^{\circ}$  and distils at  $351^{\circ}$ . Its concentrated sulphuric acid solution has a yellow color, and is colored a dark green by oxidizing agents. Its picric acid compound crystallizes in red needles, melting at  $186^{\circ}$ . Acetic anhydride converts it into an *acetate*,  $C_{12}H_8N.C_2H_3O$ , melting at  $69^{\circ}$ . Its *nitroso-derivative*,  $C_{12}H_8N.NO$ , formed when  $KNO_2$  acts upon the ethereal or alcoholic solution of carbazol, consists of long, golden yellow needles, melting at  $82^{\circ}$ . It regenerates carbazol if boiled with acids or alcohol.

The nitrogen atom in carbazol is probably joined to two ortho-positions of the two benzene nuclei of diphenyl, and with every two carbon atoms of the latter it makes a closed ring, like that contained in pyrrol (p. 399). **Phenyl-naphthyl carbazol**,  $C_{16}H_{13}N = \langle \begin{smallmatrix} C_6H_4 \\ C_{10}H_8 \end{smallmatrix} \rangle NH$ , is perfectly analogous to carbazol. It is found in the anthracene residues, and is prepared artificially from  $\beta$ -phenyl-naphthylamine,  $C_{10}H_9.NH.C_6H_5$ . It is greenish-yellow in color and melts at  $330^{\circ}$ .

**Azo-diphenylene**,  $\langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle N_2$ , is produced when the calcium azobenzoates (ortho-, meta-, para) are distilled. It sublimes in yellow needles, melting at  $170^{\circ}$ .

We obtain a mono- and a di-sulphonic acid,  $C_{12}H_9.SO_3H$ , and  $C_{12}H_8(SO_3H)_2$ , on digesting diphenyl with sulphuric acid. The first is formed with a very little sulphuric acid. The disulpho-acid (para) crystallizes in deliquescent prisms, melting at  $72.5^{\circ}$ . The oxy-diphenyls are the products on fusion with alkalis.

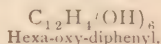
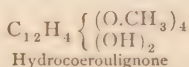
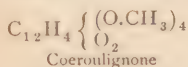
**Oxy-diphenyl**,  $C_{12}H_9.OH$ , Diphenylol, is obtained by diazotizing amido-diphenyl sulphate. It sublimes in shining leaflets, melting at  $165^{\circ}$ . It dissolves with a beautiful green color in concentrated sulphuric acid.

**Dioxydiphenyls**, *Diphenols*,  $C_{12}H_8(OH)_2$ . The para-compound,  $C_6H_4(OH)_2$ ,  $C_6H_4(OH)(\gamma)$ , is obtained from benzidine by means of the diazo-compound and by fusing diphenyl-disulphonic acid with caustic alkali. It consists of shining leaflets or needles, melting at  $272^{\circ}$  and boiling above  $360^{\circ}$ . An *isomeric* diphenol ( $\delta$ ), formed on fusing phenol-ortho- and para-sulphonic acids with potassium hydroxide (*Ber.*, 13, 2233), melts at  $161^{\circ}$ . Two additional diphenols ( $\alpha$  and  $\beta$ ) are obtained when phenol is fused with KOH; the  $\alpha$ -melts at  $123^{\circ}$  and the  $\beta$ -at  $190^{\circ}$ .

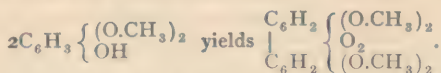
**Diphenylene Oxide**,  $C_{12}H_8O = \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle O$ , results when phenylphosphate is distilled with lime, or from calcium phenylate or phenol and lead oxide under the same treatment. It crystallizes in leaflets melting at  $81^{\circ}$  and distilling at  $287^{\circ}$ .

**Diphenylene Sulphide**,  $\langle \begin{smallmatrix} C_6H_4 \\ C_6H_5 \end{smallmatrix} \rangle S$ , is produced when phenyl sulphide and phenyl disulphide (p. 484) are distilled through an ignited tube. Shining needles or leaflets, melting at  $97^{\circ}$  and distilling at  $332^{\circ}$ . Chromic acid oxidizes it to diphenylene sulphone,  $C_{12}H_8:SO_2$ .

**Coeroulignone or Cedrilet**,  $C_{16}H_{16}O_6$ , is a derivative of hexa-oxydiphenyl:—

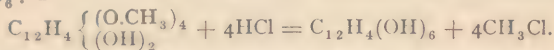


Coeroulignone separates as a violet powder when crude wood-spirit is purified on a large scale by means of potassium chromate. It is further formed on oxidizing dimethyl-pyrogallol (p. 501) with potassium chromate or ferric chloride:—



Coerulignone is insoluble in the ordinary solvents, and is precipitated in fine, steel-blue needles, from its phenol solution, by alcohol or ether. It dissolves in concentrated sulphuric acid with a beautiful blue color, resembling that of the corn-flower. Large quantities of water color the solution red at first. Reducing agents (tin and hydrochloric acid) convert coerulignone into colorless hydrocoeroulignone, which changes again to the first by oxidation. Coerulignone is, therefore, a quinone body, departs itself towards hydrocoeroulignone like quinone to hydroquinone, and hence may be called a double-nuclei quinone (p. 503).

**Hydrocoeroulignone**,  $\text{C}_{16}\text{H}_{18}\text{O}_6$ , crystallizes from alcohol and glacial acetic acid in colorless leaflets, melting at  $190^\circ$ , and distills with almost no decomposition. It is a divalent phenol. When heated with concentrated hydrochloric or hydriodic acid it breaks up into methyl chloride and **Hexaoxydiphenyl**,  $\text{C}_{12}\text{H}_{10}\text{O}_6$ :—



The latter crystallizes from water in silvery leaflets. It dissolves with a beautiful bluish-violet color in potassium hydroxide. Acetyl chloride converts it into an *hexacetate*. Diphenyl results when it is heated with zinc dust.

If potassium diphenyl-mono-sulphonate and disulphonate be heated with potassium cyanide the *nitriles*,  $\text{C}_{12}\text{H}_9.\text{CN}$  and  $\text{C}_{12}\text{H}_8(\text{CN})_2$ , result: the former melts at  $85^\circ$ , the latter at  $234^\circ$ . The corresponding diphenyl-carboxylic acids are obtained when these are saponified with alcoholic potassium hydroxide or with hydrochloric acid.

**Diphenyl-carboxylic Acid**,  $\text{C}_{13}\text{H}_{10}\text{O}_2 = \text{C}_6\text{H}_5.\text{C}_6\text{H}_4.\text{CO}_2\text{H}$  (para) is also formed when diphenyl benzene (p. 606) is oxidized with  $\text{CrO}_3$  and glacial acetic acid or phenyl tolyl (p. 606) with nitric acid. It crystallizes from alcohol in bundles of grouped needles, melting at  $218^\circ$ . It affords diphenyl on distillation with lime, and yields terephthalic acid if oxidized with a chromic acid mixture.

The isomeric **phenyl-benzoic acid**,  $\text{C}_6\text{H}_5.\text{C}_6\text{H}_4.\text{CO}_2\text{H}$  (ortho), is obtained by fusing diphenylene ketone with potassium hydroxide (p. 604). It melts at  $110$ – $111^\circ$ . It reverts to diphenylene ketone when heated with lime.

**Diphenyl-dicarboxylic Acid**,  $\left\{ \begin{array}{l} \text{C}_6\text{H}_4.\text{CO}_2\text{H} \\ \text{C}_6\text{H}_4.\text{CO}_2\text{H} \end{array} \right\}$  (dipara), is obtained from di-

phenyl-dicyanide, and by oxidizing ditolyl with chromic acid in a glacial acetic acid solution. It is an amorphous white powder, insoluble in alcohol and ether. It decomposes at higher temperatures without first fusing. Its barium and calcium salts are almost insoluble in water; the diethyl ester melts at  $112^\circ$ . Heated with lime it affords diphenyl.

The isomeric **Diphenic Acid**,  $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} \end{array}$  (diortho), is produced when

phenanthrene and phenanthraquinone are oxidized with a chromic acid mixture, the latter also by potassium permanganate or by the action of an alcoholic potassium hydroxide solution. It is very readily soluble in hot water, alcohol and ether, crystallizes in shining needles or leaflets, melting at  $229^\circ$ , and sublimes. Its barium and calcium salts are readily soluble in water. The diethyl ester melts at  $42^\circ$ . Chromic acid changes it to diphenic acid. It yields diphenyl when distilled with soda-lime. When diphenic acid is digested with acetyl chloride,  $\text{PCl}_5$  or sulphuric acid, its *anhydride*,  $\text{C}_{12}\text{H}_8(\text{CO})_2\text{O}$ , is formed. This melts at  $220^\circ$ , and when distilled decomposes into  $\text{CO}_2$  and diphenylene ketone.

A *diamido diphenic acid*,  $\text{C}_{12}\text{H}_6(\text{NH}_2)_2(\text{CO}_2\text{H})_2$ , is obtained through the molecular transposition of meta-hydrazo-benzoic acid (p. 538), and on reducing  $\alpha$ -dinitro-diphenic acid (from diphenic acid and from dinitro-phenanthraquinone). It partly melts at  $170^\circ$ , being transformed at the time into another amido-acid. Distilled with baryta or lime it yields benzidine (together with amido-fluorene). The elimination of the  $\text{NH}_2$  group causes it to change to diphenic acid. We, therefore, infer that the latter (and also Phenanthrene, see this) is a diortho-derivative of diphenyl.

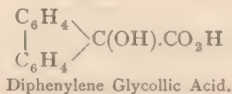
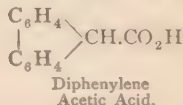
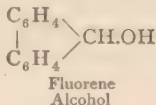
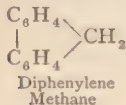
An isomeric **Isodiphenic Acid**, melting at  $216^\circ$ , has been obtained from fluoranthene (*Ann.*, 200, 20).

On heating diphenic acid (also isodiphenic acid) or phenylbenzoic acid with lime we obtain

**Diphenylene Ketone**,  $\text{C}_{13}\text{H}_8\text{O} = \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \rangle \text{CO}$ , which is also obtained by

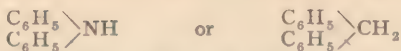
oxidizing diphenylene-methane (p. 605) with a chromic acid mixture, and by heating anthraquinone and phenanthraquinone with caustic lime (*Ann.*, 196, 45). It is very soluble in alcohol and ether, crystallizes in large yellow prisms, melting at  $84^\circ$ , and boiling at  $337^\circ$ . Being a ketone it unites with hydroxylamine to produce an *acetoxim*, melting at  $192^\circ$ . The chromic acid mixture completely destroys it, but potassium permanganate oxidizes it to phthalic acid. It is converted into phenyl benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (p. 603), on fusion with potassium hydroxide.

We also have a series of compounds, the *diphenylene derivatives*, in which 2 hydrogen atoms of the diphenyl group (both in the ortho-position with reference to the point of union of the diphenyl group, comp., *Ber.*, II, 1214) are replaced by one carbon atom. In addition to diphenylene ketone, the following bodies are classed here:—

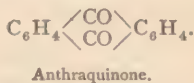
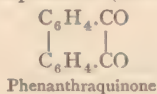
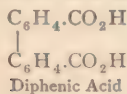


Carbazol and diphenylene oxide (p. 602), are such diphenylene-

diortho-derivatives. Intimately related to the diphenylene derivatives, *e. g.*,



they are frequently derived from the latter on heating by an ortho-condensation of the two phenyl groups with the exit of two hydrogen atoms. In diphenic acid (p. 604) the two  $\text{CO}_2\text{H}$  groups are also in the ortho-position. The acid stands in close relation to phenanthraquinone and anthraquinone (see these):—



**Diphenylene Methane**,  $\text{C}_{13}\text{H}_{10} = \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2$ , **Fluorene**, occurs in coal

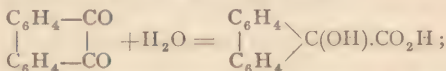
tar (boiling at  $300\text{--}305^\circ$ ) and is obtained by conducting diphenylmethane,  $(\text{C}_6\text{H}_5)_2\text{CH}_2$ , through an ignited tube, also on heating diphenylene ketone with zinc dust, or with hydriodic acid and phosphorus to  $160^\circ$ . (For the detection of fluorene in presence of phenanthrene and anthracene see *Ber.*, **11**, 203).

It crystallizes from hot alcohol in colorless leaves with a violet fluorescence, melts at  $113^\circ$ , and boils at  $295^\circ$ . It affords a compound with picric acid, which crystallizes in red needles, melting at  $80\text{--}82^\circ$ . The chromic acid mixture oxidizes it to diphenylene ketone. Fusion with KOH affords dioxydiphenyl.

**Fluorene Alcohol**,  $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH.OH}$ , results in the action of sodium amalgam

upon the alcoholic solution of diphenylene ketone and by heating sodium diphenylene glycollic acid to  $120^\circ$ . It crystallizes from hot water in fine needles, from alcohol in six-sided plates, melting at  $153^\circ$ . Chromic acid changes it back to diphenylene ketone. Concentrated sulphuric acid or  $\text{P}_2\text{O}_5$  colors it an intense blue, and produces *fluorene ether*,  $(\text{C}_{13}\text{H}_9)_2\text{O}$ , melting at  $290^\circ$ .

**Diphenylene Glycollic Acid**,  $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{C(OH).CO}_2\text{H}$ , is produced when phenanthraquinone is boiled with sodium hydroxide:—



in this instance an atomic rearrangement occurs similar to that observed in the transition of benzil to benzilic acid. It crystallizes from hot water in shining leaflets, melting at  $162^\circ$ . It dissolves with an indigo blue color in concentrated sulphuric acid; this color disappears on the addition of water.  $\text{CO}_2$  and  $\text{H}_2\text{O}$  split off and *fluorene ether* results. This is also produced by heating the acid above its melting point. Chromic acid oxidizes it to diphenylene ketone. If the acid be heated to  $120^\circ$  with HI and P it becomes,

**Diphenylene Acetic Acid**,  $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH.CO}_2\text{H}$ ,—**Fluorene Carboxylic Acid**.

This is insoluble in water, forms indistinct crystals, and melts about  $221^\circ$ . Its ethyl ester melts at  $165^\circ$ . When heated above its melting point, more readily with soda-lime, it is decomposed into  $\text{CO}_2$  and diphenylene methane.



**Phenyl Tolyl**,  $C_6H_5.C_6H_4.CH_3$  (para), is produced, like diphenyl, by the action of Na upon a mixture of brombenzene and para-brombenzene dissolved in ether. It is a liquid, boiling about  $265^\circ$ , has a sp. gr. = 1.015, and solidifies below  $0^\circ$ . It affords diphenyl carboxylic acid and terephthalic acid when oxidized.

**Ditolyl**,  $C_{14}H_{14} = CH_3.C_6H_4.C_6H_4.CH_3$  (dipara), results when sodium acts on parabrom-toluene. It is easily soluble in hot alcohol, melts at  $121^\circ$ , and distils without decomposition. It yields diphenyl dicarboxylic acid by oxidation (p. 603).

**Diphenyl Benzene**,  $C_{18}H_{14} = C_6H_4 \begin{smallmatrix} \diagup C_6H_5 \\ \diagdown C_6H_5 \end{smallmatrix}$ , Diphenyl Phenylene, is produced when sodium acts on a mixture of dibrombenzene,  $C_6H_4Br_2$  (1, 4) and  $C_6H_5Br$ , also on conducting a mixture of diphenyl and benzene through ignited tubes. **Isodiphenyl benzene** also results in the latter case; therefore, both are produced in the preparation of diphenyl (*Ber.*, **II**, 1755).

Diphenyl benzene is difficultly soluble in hot alcohol and ether, easily in benzene, crystallizes in flat needles, melts at  $205^\circ$ , sublimes readily, and boils at  $400^\circ$ .  $CrO_3$ , in glacial acetic acid, oxidizes it to diphenyl carboxylic acid (p. 603), and then to terephthalic acid. Isomeric isodiphenyl benzene melts at  $85^\circ$ , and boils about  $360^\circ$ .  $CrO_3$ , in glacial acetic acid, oxidizes it to benzoic acid and an isomeric diphenyl carboxylic acid.

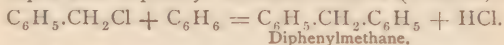
**Triphenyl Benzene**,  $C_6H_3(C_6H_5)_3$  (1, 3, 5), is formed from acetophenone,  $C_6H_5.CO.CH_3$ , when heated with  $P_2O_5$ , or by conducting HCl into it, when there occurs a condensation similar to that observed in the formation of mesitylene from acetone,  $CH_3.CO.CH_3$  (p. 410). It crystallizes from ether in rhombic plates, melting at  $169^\circ$ , and distils above  $360^\circ$ .

## 2. Derivatives of benzene nuclei joined by one carbon atom.

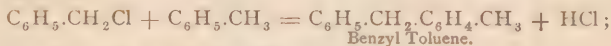
### DIPHENYL METHANE DERIVATIVES.

The compounds, having two benzene nuclei joined by one carbon atom, are obtained according to the following methods:—

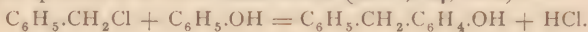
1. Zinc dust is added to a mixture of benzyl chloride and benzene, and heat applied. An energetic reaction ensues, hydrogen chloride escapes and diphenyl methane results (Zincke):—



Benzyl chloride reacts similarly upon toluene, xylene and other hydrocarbons:—



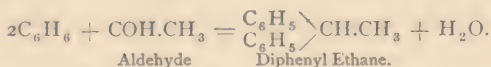
and upon phenols or their acid esters (*Ber.*, **14**, 261):—



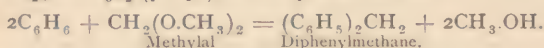
Aluminium chloride may be employed as a substitute for zinc dust (p. 412).

The tertiary anilines (compare p. 438) react similarly to the phenols on the application of heat; thus from benzyl chloride and dimethyl aniline we get the base,  $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot N(CH_3)_2$ , dimethylamido-diphenylmethane.

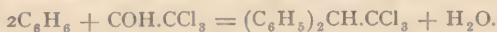
2. The fatty aldehydes are mixed with benzene (toluene, naphthalene, diphenyl, etc.) and concentrated sulphuric acid then added; water separates and two phenyls replace the aldehyde oxygen (Baeyer):—



The acetaldehyde is applied as paraldehyde, and it is necessary to employ strongly cooled sulphuric acid. Methylene aldehyde is applied in the form of methylal,  $CH_2(O \cdot CH_3)_2$  (p. 256), or methyl diacetate:—

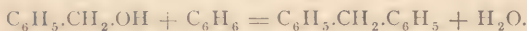


The reaction proceeds with special ease on using anhydrous chloral (or with mono- and dichlor-aldehyde) and chlorine substitution products result:—



Sodium amalgam causes the replacement of the halogens in these derivatives, and we get the corresponding hydrocarbons.

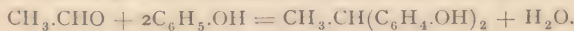
The benzene hydrocarbons react with the aromatic alcohols just as they do with the aldehydes:—



Triphenyl methane,  $(C_6H_5)_3CH$ , is similarly formed from benzhydrol,  $(C_6H_5)_2CH \cdot OH$ .

The benzenes also condense with ketones, aldehydic acids and ketonic acids. Thus from benzene and glyoxylic acid we obtain diphenylacetic acid, with pyroracemic acid,  $\alpha$ -diphenylpropionic acid. Sometimes we get an aldol condensation with the production of oxy-compounds (p. 155); in this way dibrom-atrolactic acid,  $C_6H_5 \cdot CH(OH) \langle \begin{smallmatrix} CHBr_2 \\ CO_2H \end{smallmatrix} \right.$ , results from benzene and dibrom-pyro-racemic acid.

The aldehydes also act upon the phenols, yielding phenol-derivatives of the diphenylmethanes; here it is better to substitute  $SnCl_4$  for sulphuric acid (*Ber.*, 11, 283). Thus we get diphenol ethane from paraldehyde and phenol:—

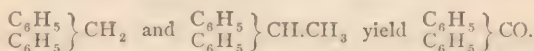


And from benzyl alcohol,  $C_6H_5 \cdot CH_2 \cdot OH$ , and phenol there results mono-oxy-diphenyl methane,  $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot OH$ . Consult *Ber.*, 16, 2835, upon the condensation of phenols with benzaldehydes.

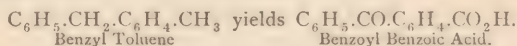
The tertiary anilines react like the phenols (p. 438) and *amido-derivatives* result. Instead of the aldehydes (or their ethers) we can employ their haloids, when the reaction will begin on the application of heat. For example,

from methylene iodide,  $\text{CH}_2\text{I}_2$ , and dimethyl aniline we obtain the base  $\text{CH}_2 \left\langle \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2 \\ \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2 \end{smallmatrix} \right\rangle$ ; the same product results with  $\text{CCl}_3\text{H}$  and  $\text{CCl}_4$ . Acetone and  $\text{ZnCl}_2$  yield the base,  $(\text{CH}_3)_2\text{C} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2 \\ \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2 \end{smallmatrix} \right\rangle$ . Such bases are also produced as by-products in the manufacture of methyl aniline and malachite green.

If the hydrocarbons be oxidized with a chromic acid mixture they yield *ketones*, and the group  $\text{CH}_2$  or  $\text{CH}$  is converted into  $\text{CO}$ . From dimethyl methane and diphenyl ethane we obtain diphenyl ketone:—

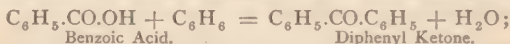


Should alkyls be present in the benzene nucleus these are oxidized to carboxyls:—



Such ketones are further produced:—

1. If benzoic acid or its anhydride be heated with benzenes and  $\text{P}_2\text{O}_5$  (*Merz*). A condensation similar to that of the hydrocarbons takes place here:—



2. By the action of benzoyl chloride on benzenes, in the presence of aluminium chloride (comp. p. 529):—



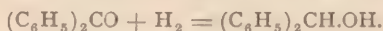
$\text{COCl}_2$  reacts in the same manner, and acid chlorides are the first products (comp. p. 529):—



3. According to the general method of producing ketones, on heating the calcium salts with aromatic acids:—

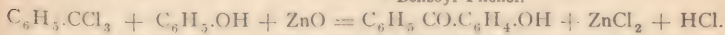
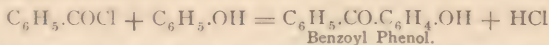


On heating with zinc dust or hydriodic acid and amorphous phosphorus, the ketones sustain a reduction of the  $\text{CO}$  group and revert to the hydrocarbons, for example, diphenyl ketone yields diphenyl methane. Sodium amalgam changes them to secondary alcohols:—



Pinacones are simultaneously produced through the union of two molecules (see benzpinacone).

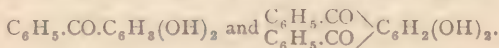
The *oxy-ketones* and *ketone phenols* are produced from the phenols by the action of benzoyl chloride, by heating with zinc chloride or more readily with aluminium chloride; further by heating benzo-trichloride,  $C_6H_5.CCl_3$ , with phenols and zinc oxide:—



The reaction is analogous to the action of chloroform upon phenols in alkaline solution, when aldehyde phenols (oxy-aldehydes) are obtained (p. 518).

Instead of the free phenols it is better to use the benzoyl esters of the phenols (e. g.,  $C_6H_5.O.C_6H_5O$ ). The first products are the benzoyl esters of the phenyl ketones, e. g.,  $C_6H_5.CO.C_6H_4.O.C_6H_5O$ , which afford the free phenol ketones when saponified with alcoholic potassium hydroxide (*Ber.*, 10, 1963). In the use of the free phenols we get, on the contrary (especially with  $C_6H_5.CCl_3$ , even by gentle digestion), coloring substances, which belong to the amine series, and are derived from triphenyl methane.

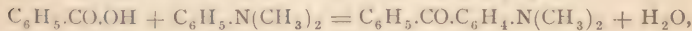
When benzoyl chloride and  $ZnCl_2$  act on the divalent phenols (their benzoyl esters) e. g., resorcin, we obtain their mono- and di-ketones (*Ber.*, 12, 661), as—



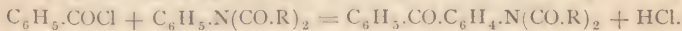
Zinc chloride converts salicylic acid,  $C_6H_4(OH).CO_2H$ , and phenol into salicyl-phenol,  $C_6H_4(OH).CO.C_6H_4.OH$  (*Ber.* 14, 656).

We can also derive the *amido-ketones*, e. g.,  $C_6H_5.CO.C_6H_4.NH_2$ , by methods similar to those employed with the ketones and oxy-ketones:—

1. By heating benzoic acid with tertiary anilines and  $P_2O_5$ :—

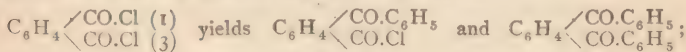


whereas, by the action of benzoyl chloride two benzoyl groups enter the benzene nucleus (*Ann.*, 206, 88); 2. by the action of benzoyl chloride upon primary anilines, in which both amide hydrogens are replaced by acid radicals (as in phthalanile,  $C_6H_5.N(CO)_2C_6H_4$ , p. 443) on heating alone or with  $ZnCl_2$  or  $AlCl_3$ :—



The free amido-ketones are obtained by the saponification of these anilides (*Ber.*, 14, 1836).

Furthermore, *ketonic acids* are produced according to these methods. For example, we obtain meta-benzoyl benzoic acid,  $C_6H_5.CO.C_6H_4.CO_2H$ , from benzoyl chloride and benzoic anhydride, with  $ZnCl_2$  (*Ber.*, 14, 647); and meta-benzoyl benzoic acid together with so-called isophthalphenone (*Ber.*, 13, 321) from isophthalic chloride and benzene by means of  $AlCl_3$ :—



ortho-benzoylbenzoic acid is obtained from phthalic anhydride and benzene with  $AlCl_3$  (p. 613).

**Diphenyl Methane**,  $C_{12}H_{12} = C_6H_5.CH_2.C_6H_5$ , Benzyl benzene, is obtained according to the synthetic methods already mentioned: from benzyl chloride and benzene with zinc dust or  $AlCl_3$ ;



from formic aldehyde or benzyl alcohol and benzene with sulphuric acid; and from  $\text{CHCl}_2$  (or  $\text{CHCl}_3$ ) with benzene and  $\text{AlCl}_3$  (together with anthracene).

In the preparation of diphenyl methane, 10 parts of benzyl chloride are digested with 6 parts of benzene and zinc dust, etc.; the latter only induces the reaction and when this has commenced it can be filtered off (*Ann.*, 159, 374). A better method is that of Friedel. It consists in digesting 10 parts benzyl chloride with 50 parts benzene and 3-4 parts  $\text{AlCl}_3$ .

Diphenyl methane is easily soluble in alcohol and ether, possesses the odor of oranges, crystallizes in needles, melts at  $26.5^\circ$ , and boils at  $262^\circ$ . When conducted through ignited tubes it yields diphenylene methane (p. 605); a chromic acid mixture oxidizes it to diphenyl ketone.

When treated with bromine in the heat it yields  $(\text{C}_6\text{H}_5)_2\text{CHBr}$ , Diphenylbrom-methane, and  $(\text{C}_6\text{H}_5)_2\text{CBr}_2$ ; the former melts at  $45^\circ$ , and boils without decomposition. Diphenyl methane dissolves in concentrated nitric acid yielding two dinitro-derivatives, the  $\alpha$ - melting at  $183^\circ$ , and the  $\beta$ - variety at  $118^\circ$ .

The reduction of the  $\alpha$  dinitro-product yields  $\alpha$ -Diamido-diphenyl methane,  $(\text{C}_6\text{H}_4\text{NH}_2)_2\text{CH}_2$  (dipara); shining leaflets, melting at  $85^\circ$ . Its tetramethyl derivative  $[(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_2\text{CH}_2]$  results from dimethyl aniline by means of  $\text{CH}_2\text{I}_2/\text{CCl}_3\text{H}$  and  $\text{CCl}_4$ , or with methylal (p. 608), and as a by-product in the manufacture of malachite green. It crystallizes in shining leaves, melts at  $90^\circ$ , and distils undecomposed.

**Oxy-diphenyl Methane**,  $\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_4\text{OH}$  (para-), Benzyl phenol, obtained from benzyl chloride and phenol, melts at  $80-81^\circ$ .

**Dioxyphenyl Methane**,  $\text{CH}_2(\text{C}_6\text{H}_4\text{OH})_2$  (dipara), is produced on fusing diphenyl methane disulphonic acid with  $\text{KOH}$ . It crystallizes in shining leaflets or needles, melts at  $158^\circ$  and sublimes. By stronger heating with  $\text{KOH}$  ( $300^\circ$ ), it decomposes into para-oxybenzoic acid and phenol. Its dimethyl ether,  $\text{CH}_2(\text{C}_6\text{H}_4\text{OCH}_3)_2$ , is formed from anisol and methylal, and melts at  $52^\circ$ .

**Diphenyl Carbinol**,  $(\text{C}_6\text{H}_5)_2\text{CH.OH}$ , Benzhydrol, is produced on heating diphenyl brom-methane,  $(\text{C}_6\text{H}_5)_2\text{CHBr}$ , with water to  $150^\circ$ , more readily from diphenyl ketone  $(\text{C}_6\text{H}_5)_2\text{CO}$ , with sodium amalgam, or by heating with alcoholic potassium hydroxide and zinc dust (together with benzpinacene). It is difficultly soluble in water, easily in alcohol and ether, crystallizes in silky needles, melts at  $68^\circ$ , and boils at  $298^\circ$  under partial decomposition into water, and benzhydrol ether  $[(\text{C}_6\text{H}_5)_2\text{CH}]_2\text{O}$ , melting at  $109^\circ$ .

**Benzophenone**, Diphenyl Ketone,  $(\text{C}_6\text{H}_5)_2\text{CO}$ , is obtained according to the general methods and by heating mercury phenyl  $(\text{C}_6\text{H}_5)_2\text{Hg}$ , with benzoyl chloride. It is prepared (along with benzene) on distilling calcium benzoate, or from benzoyl chloride and benzene with  $\text{AlCl}_3$ . It is dimorphous; generally crystallizes in large rhombic prisms, melting at  $48-49^\circ$ , sometimes in rhombohedra, which melt at  $27^\circ$  and gradually change to the first modification. It has an aromatic odor, and boils at  $295^\circ$ . When fused with alkalis it decomposes into benzoic acid and benzene; if it be heated with zinc dust diphenyl methane is produced.  $\text{PCl}_5$  converts it into the chloride  $(\text{C}_6\text{H}_5)_2\text{CCl}_2$ . Its phenyl hydrazine compound melts at  $137^\circ$ .

**Amidobenzophenone**,  $C_6H_5.CO.C_6H_4(NH_2)$  (para), benzoaniline, from benzoyl chloride, phthanile and  $ZnCl_2$  (p. 609), melts at  $124^\circ$ .

**Diamidobenzophenones**,  $CO(C_6H_4.NH_2)_2$ , are formed by reducing dinitrobenzophenones. Tetramethyl-diamido-benzophenone has been obtained from dimethyl aniline with  $COCl_2$ , and melts at  $179^\circ$ . It yields methyl violet with dimethyl aniline (and  $PCl_3$ ).

**Oxybenzophenone**,  $C_6H_5.CO.C_6H_4(OH)$  (para), is obtained from amidobenzophenone with nitrous acid, and from phenol with benzoyl chloride or  $C_6H_5.CCl_3$  (p. 609). It melts at  $134^\circ$ , and when fused with KOH decomposes into benzene and para-oxybenzoic acid.

**Dioxybenzophenone**,  $CO(C_6H_4.OH)_2$  (dipara), is obtained from dioxydiphenyl methane by oxidizing the dibenzoyl ester with  $CrO_3$  in glacial acetic acid and saponifying with alkalis; also by the decomposition of aurin, benzaurin, phenolphthalein, and rosaniline (*Ber.*, 16, 1931) on heating with water or caustic alkali. It crystallizes from hot water in needles or leaflets, melts at  $210^\circ$ , and decomposes on fusion with KOH into para-oxy-benzoic acid and phenol. It yields an *acetoxim* with hydroxylamine. It condenses with phenol (and  $PCl_3$ ) to aurin.

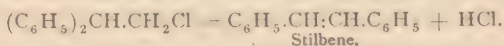
So-called **Diphenylene Ketone Oxide**,  $CO\langle C_6H_4 \rangle O$  (?), is produced from sodium salicylate with  $POCl_3$  and by distilling salicylide. It forms yellow needles, melting at  $173^\circ$ . When reduced with HI it affords *methylene-diphenyl oxide*,  $CH_2(C_6H_4)_2O$ , obtained by the reduction of euxanthone with zinc dust, and when oxidized again yields diphenylene ketone oxide. As the latter does not unite with hydroxylamine it must have another constitution (*Ber.*, 17, 808).

**Diphenyl Ethane**,  $C_{14}H_{14} = (C_6H_5)_2CH.CH_3$  (isomeric with dibenzyl), is obtained from benzene and paraldehyde with sulphuric acid, from  $\beta$ -bromethyl benzene,  $C_6H_5.CHBr.CH_3$ , and benzene with zinc dust, from benzene and  $CH_3.CHCl_2$  with  $AlCl_3$ . It is a liquid, boiling at  $268-271^\circ$ , and in the cold becomes a crystalline solid. Chromic acid oxidizes it to benzophenone. **Diphenyl trichlorethane**,  $(C_6H_5)_2CH.CCl_3$ , formed from benzene and chloral, consists of leaflets, melting at  $64^\circ$ . *Diphenyltribromethane* melts at  $89^\circ$ . Sodium amalgam reduces both to diphenyl ethane.

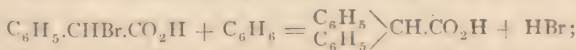
Mono-chlor-aldehyde (mono-chlor-acetal or dichlorether, p. 155) and benzene yield **Diphenyl mono-chlor-ethane**,  $(C_6H_5)_2CH.CH_2Cl$ , a thick oil, which on boiling is converted into

**Diphenyl Ethylene**,  $C_{14}H_{12} = (C_6H_5)_2C:CH_2$ . This is isomeric with stilbene, is also formed from  $\alpha$ -dibrom-ethylene,  $CH_2:CHBr$ , by means of benzene and  $AlCl_3$ , and is an oil, boiling at  $277^\circ$ . Chromic acid oxidizes it to diphenyl ketone.

Perfectly analogous, unsaturated hydrocarbons are also obtained from toluene, xylene, naphthalene, etc. If diphenyl monochlorethane (or its analogues) be heated alone HCl is withdrawn, and there results, not diphenyl ethylene, but, by molecular transposition, isomeric stilbene (and its analogues):—



**Diphenyl Acetic Acid**,  $C_{14}H_{12}O_2 = (C_6H_5)_2CH.CO_2H$ , is formed: by the action of zinc dust on a mixture of phenyl-bromacetic acid (p. 540) and benzene:



from diphenyl brom-methane,  $(C_6H_5)_2CHBr$ , by means of the cyanide; and by

heating benzoic acid to  $150^{\circ}$  with hydriodic acid. The acid crystallizes from water in needles, from alcohol in leaflets, melting at  $146^{\circ}$ . When oxidized with a chromic acid mixture it yields benzophenone; and when heated with soda lime we get diphenyl methane. Its ethyl ester melts at  $58^{\circ}$ . Diphenyl acetic acid can also be obtained by the condensation of  $2C_6H_6$  with glyoxylic acid,  $CHO \cdot CO_2H$ , by means of sulphuric acid (p. 607). In the same manner benzene and

pyrroacemic acid yield  $\alpha$ -Diphenyl-propionic Acid,  $(C_6H_5)_2C \begin{smallmatrix} \diagup CH_3 \\ \diagdown CO_2H \end{smallmatrix}$  diphenyl methyl acetic acid, melting at  $171^{\circ}$ , and distilling at  $300^{\circ}$ .

**Diphenyl Glycollic Acid, Benzilic Acid**,  $(C_6H_5)_2C(OH)CO_2H$ , is produced by a molecular rearrangement of benzil (see this) when digested with alcoholic potassium hydroxide, and from diphenyl acetic acid by the action of bromine vapor and boiling with water. We can prepare it by fusing benzil with KOH (*Ber.*, 14, 326). Perfect analogues of benzilic acid are anisilic, cuminilic and dibenzyl glycollic (see benzoïn group) acids.

Benzilic acid is very readily soluble in hot water and alcohol, crystallizes in needles and prisms, melts at  $150^{\circ}$ , and is of a deep red color. It dissolves with a dark red color in sulphuric acid. It yields diphenyl acetic acid when heated with HI; on distilling its barium salt it breaks up into  $CO_2$  and benzyhydro (p. 610); oxidation yields benzophenone.

**Benzyl Toluenes, Phenyl tolyl methanes**,  $C_{14}H_{14} = C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot CH_3$ . A liquid mixture of ortho- and para-benzyl toluene, which cannot be separated, is obtained by the action of zinc dust on a mixture of benzyl chloride and toluene; by heating benzyl chloride to  $190^{\circ}$  with water, or toluene to  $250^{\circ}$  with iodine. The pure *para*-body has been formed by heating para-phenyl tolyl ketone with zinc dust, and is a liquid, boiling at  $285^{\circ}$ .

When it is oxidized with a chromic acid mixture we get the corresponding phenyl tolyl ketones and benzoyl benzoic acids.

**Phenyl-tolyl ketones**,  $C_{14}H_{12}O = C_6H_5 \cdot CO \cdot C_6H_4 \cdot CH_3$ . A mixture of the ortho- and para-compounds is obtained when benzoyl chloride and toluene are heated with zinc dust (in small quantity), by the distillation of a mixture of calcium benzoate and para-toluate, or by heating benzoic acid and toluene with  $P_2O_5$ . The product is an oil, from which the para-body may be crystallized out by cooling, while the ortho-derivative remains liquid.

The *para* compound is dimorphous, crystallizing in hexagonal prisms, melting at  $55^{\circ}$ , and in monoclinic prisms, melting at  $58-59^{\circ}$ . The latter modification is the more stable. It boils at  $310-312^{\circ}$ , and is difficultly soluble in alcohol. When heated with soda lime it decomposes into benzene and paratoluic acid; chromic acid converts it into parabenzoyl benzoic acid. Sodium amalgam transforms para-ketone into phenyl paratolyl carbinol,  $\begin{smallmatrix} C_6H_5 \\ C_7H_7 \end{smallmatrix} \rangle CH.OH$ , consisting of shining needles, melting at  $52^{\circ}$ .

**Phenyl-ortho-tolyl Ketone** is a liquid and boils about  $316^{\circ}$ .

A characteristic feature is the ability of the ortho-, but not the para-derivatives, to change readily to anthracene and its derivatives, in consequence of an ortho-condensation of the two benzene nuclei (p. 605). Thus anthracene is produced in conducting phenyl-



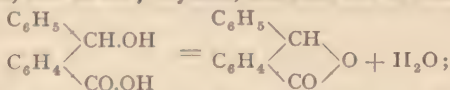
tolyl methane through an ignited tube or upon heating the ketone with zinc dust, and we obtain anthraquinone (see anthracene) on heating ortho-phenyl-tolyl-ketone with lead oxide.

**Benzoyl Benzoic Acids**,  $C_{13}H_{10}O_4 = C_6H_5 \cdot CO \cdot C_6H_4 \cdot CO_2H$ , result from the oxidation of the phenyl tolyl methanes or phenyl-tolyl ketones, and can be synthesized by the methods given upon p. 609.

The *para* acid crystallizes and sublimes in leaflets, melting at  $194^\circ$ . The *meta* acid, from isophthalic chloride and benzene, consists of needles, melting at  $161^\circ$ . The *ortho*-acid is most readily obtained from phthalic anhydride, benzene and  $AlCl_3$  (p. 609). It crystallizes from water with 1 molecule  $H_2O$ , which is lost at  $110^\circ$ , and it then melts at  $127^\circ$ . Heated to  $180^\circ$  with  $P_2O_5$ , water is eliminated, and anthraquinone is produced; in the same manner we get anthraquinone sulphonic acid by digestion with fuming sulphuric acid. With benzene and  $AlCl_3$  orthobenzoyl-benzoic acid yields phthalophenone, with phenol and  $SnCl_4$  oxyphthalophenone (see phthaleins).

If zinc and hydrochloric acid or sodium amalgam be allowed to act on the alcoholic solution of the *para*-acid we obtain **Para-benzhydryl-benzoic Acid**,  $C_6H_5 \cdot CH(OH) \cdot C_6H_4 \cdot CO_2H$ , melting at  $165^\circ$ , and passing back into benzoyl benzoic acid when oxidized. Heated to  $160^\circ$  with hydriodic acid, it affords **benzyl benzoic acid**,  $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ , which is also produced in small quantity from benzyl toluene by oxidation with nitric acid. This melts at  $157^\circ$ , and is rather readily soluble in hot water. Chromic acid oxidizes it to benzoyl benzoic acid. Diphenyl methane is produced on heating it with soda-lime.

In the same manner ortho-benzoyl benzoic acid affords **ortho-benzhydryl-benzoic acid**,  $C_6H_5 \cdot CH(OH) \cdot C_6H_4 \cdot CO_2H$ , by reduction. This acid, however, does not exist in a free condition, but at the moment of its liberation from its salts decomposes, like all the  $\gamma$ -oxyacids, into water and its lactone:—



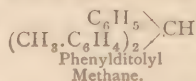
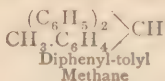
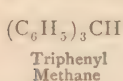
this is similar to the formation of phthalid (p. 552), from ortho-oxyethyl benzoic acid. The lactone,  $C_{14}H_{10}O_2$ , is insoluble in water, crystallizes from hot alcohol and ether in needles, and melts at  $115^\circ$ . Only after protracted warming with alkalis can it be transformed into salts of orthobenzhydryl-benzoic acid. Like orthophenyl-tolyl ketone and ortho-benzyl benzoic acid, it is easily changed into anthraquinone.

**Ditolyl Methane**,  $CH_2 \begin{array}{c} \swarrow C_6H_4 \cdot CH_3 \\ \searrow C_6H_4 \cdot CH_3 \end{array}$ , **Ditolyl Ketone**,  $CO \begin{array}{c} \swarrow C_6H_4 \cdot CH_3 \\ \searrow C_6H_4 \cdot CH_3 \end{array}$ , **Ditolyl Ethane**,  $CH_3 \cdot CH(C_6H_4 \cdot CH_3)_2$ , etc., are produced similar to the phenyl compounds and yield exactly corresponding derivatives. Ditolyl chlor-ethane,  $CH_2Cl \cdot CH(C_6H_4 \cdot CH_3)_2$ , yields on the one hand (by alcoholic potash) ditolyl ethylene,  $CH_2 : C(C_6H_4 \cdot CH_3)_2$ , upon the other by aid of heat (through molecular rearrangement) dimethyl stilbene,  $CH_3 \cdot C_6H_4 \cdot CH : CH \cdot C_6H_4 \cdot CH_3$  (comp. p. 611).



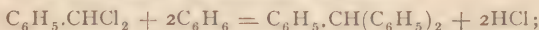
## TRIPHENYL METHANE DERIVATIVES.

These contain three benzene nuclei attached to 1 carbon-atom :—

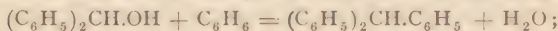


These are the parent hydrocarbons from which originate the rosaniline dyes, the malachite-greens, the aurins and phthaleins. They may be synthesized by methods analogous to those employed with the diphenyl methane derivatives :—

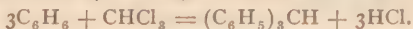
1, from benzal chloride,  $\text{C}_6\text{H}_5 \cdot \text{CHCl}_2$  (or  $\text{C}_6\text{H}_5 \cdot \text{CCl}_3$ ) and the benzenes with zinc dust or aluminium chloride :—



2, from benzhydrol (p. 610), and the benzenes with  $\text{P}_2\text{O}_5$  :—



3, from chloroform (or  $\text{CCl}_4$ ) and benzene with  $\text{AlCl}_3$  :—



A better means is the condensation of benzaldehyde with anilines (their salts) and phenols, in which we have produced amido- and phenol-derivatives of triphenyl methane (p. 617). Sulphuric acid, zinc chloride, potassium bisulphate (*Ber.*, 16, 2541), and anhydrous oxalic acid serve as reagents to induce the condensation (*Ber.*, 17, 1078).

**Triphenyl Methane**,  $(\text{C}_6\text{H}_5)_3\text{CH} = \text{C}_{19}\text{H}_{16}$ , is the product of the reaction between benzal chloride,  $\text{C}_6\text{H}_5 \cdot \text{CHCl}_2$ , and mercury diphenyl,  $\text{Hg}(\text{C}_6\text{H}_5)_2$ , and is most easily prepared from chloroform and benzene, aided by  $\text{AlCl}_3$ .

*Preparation.*—One part of  $\text{AlCl}_3$  is gradually added to a mixture consisting of one part of chloroform and five parts of benzene, and the temperature raised to  $60^\circ$ , until the evolution of hydrogen chloride ceases (30 hours). The product is poured into water, and the oil, which separates, is fractionated. Diphenyl methane is produced at the same time (*Ann.*, 194, 252, and *Ber.*, 15, 361). It is furthermore obtained from diamido- and triamido-triphenyl methane, by dissolving the latter in sulphuric acid, introducing nitrous acid and boiling with alcohol (p. 458, and *Ann.*, 206, 152).

Triphenyl methane is difficultly soluble in cold alcohol and glacial acetic acid, easily in ether, benzene and hot alcohol, crystallizing from the latter in shining, thin leaflets, melting at  $93^\circ$ , and distilling about  $355^\circ$ . It crystallizes from hot benzene in large prisms, containing two molecules of benzene, and melts at  $75^\circ$ , and when exposed to the air parts with benzene and falls into a white powder.

Bromine converts triphenyl methane (dissolved in  $\text{CS}_2$ ) into the bromide,  $(\text{C}_6\text{H}_5)_3\text{CBr}$ , melting at  $152^\circ$ .  $\text{PCl}_5$  converts the carbinol into the chloride,

melting about  $105^{\circ}$ . When heated over  $200^{\circ}$  both decompose into the halogen hydride and **Diphenylene phenyl methane**,  $\begin{matrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{matrix} \text{CH.C}_6\text{H}_5$ , which can also be obtained from fluorene alcohol (p. 605) and benzene by means of  $\text{SO}_4\text{H}_2$ . It melts at  $146^{\circ}$ . Potassium cyanide converts the chloride into a cyanide, which yields **Triphenyl-acetic Acid**,  $(\text{C}_6\text{H}_5)_3\text{C.CO}_2\text{H}$ , melting about  $260^{\circ}$ , with decomposition.

On boiling the bromide or chloride with water we get **Triphenyl carbinol**,  $(\text{C}_6\text{H}_5)_3\text{C.OH}$ , which is more readily obtained by the direct hydroxylation of triphenyl methane. This is accomplished by digesting the latter with  $\text{CrO}_3$  in a glacial acetic acid solution (*Ber.*, 14, 1944). It is very readily soluble in alcohol, ether and benzene, crystallizes in shining prisms, melting at  $159^{\circ}$ , and distilling above  $360^{\circ}$  without decomposition. It is decomposed when nitrated.

When triphenyl methane is dissolved in fuming nitric acid (sp. gr. 1.5) it becomes a trinitro-derivative,  $\text{CH}(\text{C}_6\text{H}_4.\text{NO}_2)_3$ , which crystallizes from glacial acetic acid and hot benzene in yellow scales, and melts at  $206^{\circ}$ . By the reduction of the nitro-groups (with zinc dust and glacial acetic acid) we obtain **paraleucaniline**,  $\text{CH}(\text{C}_6\text{H}_4.\text{NH}_2)_3$  (p. 618). By the hydroxylation of the tertiary hydrogen atom of trinitrophenyl methane (by digestion with  $\text{CrO}_3$  in glacial acetic acid) we get **Trinitrotriphenyl Carbinol**,  $(\text{C}_6\text{H}_4.\text{NO}_2)_3\text{C.OH}$ , which separates from benzene or glacial acetic acid in small, colorless crystals, melting at  $171-172^{\circ}$ , and when the nitro-groups are reduced (with a little zinc dust and glacial acetic acid) it is transformed into **pararosaniline**,  $(\text{C}_6\text{H}_4.\text{NH}_2)_3\text{C.OH}$  (p. 619).

#### **Diphenyl-tolyl Methanes**, $(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_4.\text{CH}_3)$ .

The para-compound is obtained from phenyl-paratolyl-carbinol (p. 612) and benzene, and also from benzhydrol,  $(\text{C}_6\text{H}_5)_2\text{CH.OH}$ , and toluene with  $\text{P}_2\text{O}_5$ . It crystallizes in thin prisms, melts at  $71^{\circ}$ , and distils above  $360^{\circ}$ . It yields a carbinol,  $\text{C}_{20}\text{H}_{15}\text{O}$ , and an acid,  $\text{C}_{20}\text{H}_{16}\text{O}_3$ , when oxidized. The trinitro-compound of diphenyl-para-tolyl methane yields on reduction of the nitro- to amido-groups, and further oxidation, bluish-violet coloring substances which differ from ordinary **rosaniline** (*Ann.*, 194, 264).

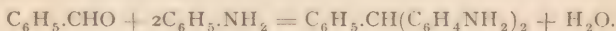
Isomeric **Diphenyl-meta-tolyl Methane**,  $(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_4.\text{CH}_3)$ , is the parent hydrocarbon of ordinary leucaniline (the triamido-compound), and is obtained from the latter by replacing the  $3\text{NH}_2$  groups by hydrogen. This is effected through the diazo-compound, (*Ann.*, 194, 282). It dissolves readily in ether, benzene and ligroïne, with difficulty in cold alcohol and wood-spirit; crystallizes in spherical aggregations of united prisms, melting at  $59.5^{\circ}$ , and distilling undecomposed above  $360^{\circ}$ . Oxidized with chromic acid in a glacial acetic acid solution it passes into *diphenyl-metatolyl-carbinol*,  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})(\text{C}_6\text{H}_4.\text{CH}_3)$ , melting at  $150^{\circ}$ .

It dissolves in fuming nitric acid with formation of a trinitro-derivative, yielding on reduction common leucaniline, which is oxidized (on heating with a few drops of hydrochloric acid), to **rosaniline** (p. 619).

*Amido-derivatives of the Triphenyl Methanes.*

**Amido-triphenyl Methane**,  $(C_6H_5)_2CH(C_6H_4.NH_2)$ , is obtained from benzhydrol,  $(C_6H_5)_2CH.OH$ , and  $HCl$ -aniline, on heating with  $ZnCl_2$  to  $150^\circ$ . It crystallizes in leaflets or prisms, melting at  $84^\circ$ . Its dimethyl compound  $(C_6H_5)_2CH.C_6H_4.N(CH_3)_2$ , is obtained from benzhydrol and dimethyl aniline upon heating with  $P_2O_5$ , also on digesting benzophenone chloride,  $(C_6H_5)_2CCl_2$  with dimethyl aniline. It crystallizes from alcohol in colorless needles or prisms melting at  $132^\circ$ . It does not afford a coloring substance by its oxidation. (*Ann.* 206, 144 and 155.)

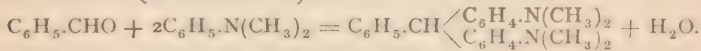
**Diamido-triphenyl Methane**,  $C_6H_5.CH(C_6H_4.NH_2)_2$ , the parent substance of malachite-green, is obtained from benzal chloride,  $C_6H_5.CHCl_2$ , and aniline with zinc dust (p. 614), or more easily from benzaldehyde with aniline hydrochloride on heating with  $ZnCl_2$  to  $120^\circ$ , and boiling the first formed product with dilute sulphuric acid. If aniline sulphate be applied we get the diamido-base directly (*Ber.*, 15, 676):—



It crystallizes from benzene with 1 molecule  $C_6H_6$  in shining prisms or spherical aggregations, melting at  $106^\circ$ , and parting with benzene at  $110^\circ$ . The free base, crystallized from ether, melts at  $139^\circ$ . It yields colorless salts with two equivalents of the acids. By their oxidation we can obtain a violet dye-stuff, *benzal violet*, with a constitution analogous to that of the rosanilines (*Ann.*, 206, 161). If the base be diazotized and boiled with water it is converted into dioxy-triphenyl-methane,  $C_6H_5.CH(C_6H_4.OH)_2$ ; the decomposition of the diazo-compound by alkalies produces triphenyl-methane (*Ann.*, 206, 152).

On methylating diamidotriphenyl-methane by heating with methyl iodide and wood-spirit to  $110^\circ$  we obtain

**Tetramethyl-diamido-triphenyl Methane**,  $C_6H_5.CH[C_6H_4.N(CH_3)_2]_2$ , leucomalachite-green, which is obtained directly from benzaldehyde (or benzal chloride) and dimethyl aniline with zinc chloride (or oxalic acid):—

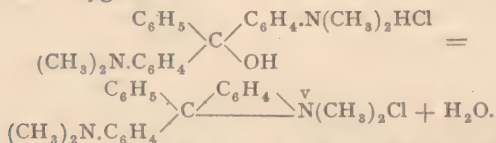


Leucomalachite-green is dimorphous, and crystallizes in leaflets, melting at  $93-94^\circ$ , or in needles, which melt at  $102^\circ$ . The first modification is obtained pure by crystallization from alcohol, the second from benzene. It yields colorless salts with two equivalents of the acids, and with  $2CH_3I$  forms an ammonium iodide. The free base oxidizes, even in the air, more readily by oxidizing agents ( $MnO_2$  and dilute sulphuric acid in the cold, or chloraniline) and becomes

**Tetramethyl-diamido-triphenyl Carbinol**,  $C_6H_5.C(OH)[C_6H_4.N(CH_3)_2]_2$ , which is the basis of malachite-green. It is obtained from its salts (malachite-green) by precipitation with the

alkalies. Free carbinol crystallizes from ligroïne in colorless needles or spherical aggregations, melting at  $130^{\circ}$ , and decomposes on stronger heating. Reduction with zinc and hydrochloric acid converts it again into leucomalachite-green.

The free base affords almost colorless solutions with acids in the cold; upon standing, more rapidly on heating, the solution acquires a green color and then contains the green salts of the anhydro-base—malachite-green. It is very probable that the salts of the carbinol are first produced, but by an inner condensation water is eliminated and they change to dye-salts (malachite-greens) (*Ber.*, 12, 2348) free from oxygen:—



Of these salts the double salt with zinc chloride,  $3(\text{C}_{23}\text{H}_{25}\text{N}_2 \cdot \text{Cl}) \cdot 2\text{ZnCl}_2 + 2\text{H}_2\text{O}$ , and the oxalate,  $2\text{C}_{23}\text{H}_{24}\text{N}_2 \cdot 3\text{C}_2\text{H}_2\text{O}_4$ , form the commercial *malachite-green* or *Victoria green*. They are mostly soluble in water, and crystallize in large, greenish prisms or plates. Their solutions impart an intense emerald-green to animal tissue, and also to vegetable fibre previously mordanted. The alkalies precipitate the colorless carbinol base from the salts.

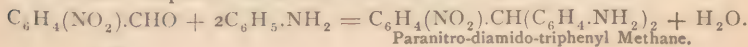
Malachite-green is obtained by oxidizing leucomalachite-green, prepared from benzaldehyde (p. 616), hence called *aldehyde green* (O. Fischer), or more directly, though less advantageously, on heating benzo-trichloride with dimethyl aniline and zinc chloride (Doebner):—



Benzoyl chloride,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{Cl}$ , and benzoic anhydride (*Ann.*, 206, 137) are similarly condensed with dimethyl aniline to malachite-green. Benzaldehyde forms perfectly analogous green coloring substances with diethyl aniline and methyl diphenylamine,  $(\text{C}_6\text{H}_5)_2\text{N} \cdot \text{CH}_3$ . It reacts in the same way with ortho- and meta-dimethyl toluidine, whereas no condensation product is furnished by the para dimethyl toluidine. The base from meta-toluidine does not yield a coloring substance when oxidized (*Ann.*, 206, 140). Salicylic aldehyde and paraoxybenzaldehyde afford green coloring substances. Furthermore, *nitromalachite-greens* have been prepared from meta-, para-, and ortho-nitrobenzaldehydes with dimethyl aniline. They are perfectly analogous to ordinary malachite-green (*Ber.*, 15, 682).

The Diphenyl-diamido-triphenyl Carbinol, obtained from diphenylamine and benzo-trichloride, and called *viridin*, readily yields a sulpho-acid. The alkali salts of this acid constitute the so-called *alkali green* (*Ber.*, 15, 1580).

**Para-nitro-diamido-triphenyl Methane**, like diamido-triphenyl methane (p. 616), is obtained from paranitrobenzaldehyde and aniline sulphate when heated with zinc chloride:—



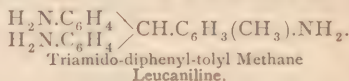
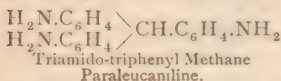
Paranitro-diamido-triphenyl Methane.



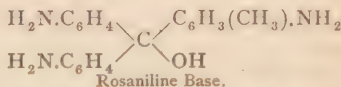
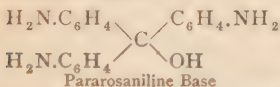
On reduction with zinc and acetic acid this yields triamido-triphenyl methane ( $C_6H_4.NH_2)_3CH$ , *paraleucaniline*.

**Meta-nitro-diamido-triphenyl Methane**, similarly obtained from meta-nitro-benzaldehyde, melts at  $136^\circ$ , and by reduction affords pseudo-leucaniline,  $CII(C_6H_4.NH_2)_3$ , isomeric with *paraleucaniline*; in it the amido-group assumes the meta-position in one benzene nucleus, whereas, in all other diamido- and triamido-triphenyl methanes, the amide groups occupy the para-position (p. 619). It oxidizes to a violet coloring substance. *Ortholeucaniline*, from *ortho*-nitro-benzaldehyde, is oxidized to a brown coloring substance (*Ber.*, 16, 1305).

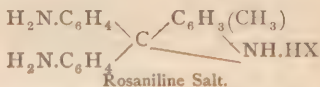
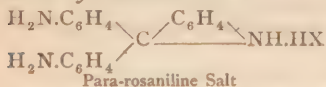
### TRIAMIDO-TRIPHENYL METHANES. ROSANILINES.



From these originate the *rosaniline* coloring substances, in a manner similar to the derivation of *benzal violet* and *malachite green* from diamidotriphenyl methane (p. 616). By their oxidation (adding hydroxyl to the CH-group) we get the carbinols or free *rosaniline bases* :—



which alone are colorless, but yield salts with the acids by exit of water (analogous to the *malachite-green* base) and give us the *rosaniline dye-substances* :—



By the replacement of the hydrogen of the amido-groups in the salts by alkyls or phenyls, the different colored *rosaniline* dyes result. The common and first discovered *rosanilines* are derived from diphenyl-meta-tolyl methane,  $C_{20}H_{18}$  (p. 615), and the carbinol base,  $C_{20}H_{20}(OH)N_3$ , and can also be called salts of the anhydride base,  $C_{20}H_{19}N_3$ ; the latter is unstable in a free state, and when liberated from its salts by alkalis, absorbs water and changes immediately to the carbinol base. The derivatives of triphenyl methane,  $C_{19}H_{16}$ , and of the base,  $C_{19}H_{18}(OH)N_3$  or  $C_{19}H_{17}N_3$  are termed *pararosanilines*, to distinguish them from those *rosanilines* just mentioned. The *colorless* salts obtained by the reduction of the *rosanilines* form bases,  $C_{19}H_{19}N_3$  and  $C_{20}H_{21}N_3$ , called *leucanilines*.

**Triamido-triphenyl Methane**,  $C_{19}H_{19}N_3 = CH(C_6H_4.NH_2)_3$ . **Paraleucaniline**, is obtained from trinitro-triphenyl methane (p. 615) and from para-nitro-diamidotriphenyl methane (p. 617) by reduction with zinc dust and acetic acid, also from para-

rosaniline with zinc dust and hydrochloric acid. It is thrown out of its salts as a white flocculent precipitate. When its diazo-compound,  $C_{19}H_{13}(N_2Cl)_3$ , is decomposed by alcohol, it yields triphenyl methane,  $C_{19}H_{16}$ . Pararosaniline is the oxidation product of para-leucaniline. Pseudo-leucaniline affords a violet, and ortho-leucaniline a brown coloring substance when oxidized (p. 618).

**Pararosaniline.** The free base,  $C_{19}H_{19}N_3O = (NH_2.C_6H_4)_3C.OH$ , or its salts,  $C_{19}H_{17}N_3.HX$  (see above), result in the oxidation of para-leucaniline and in the reduction of trinitrophenyl carbinol (p. 615), with a little zinc dust and glacial acetic acid. It is most easily made by oxidizing a mixture of aniline and paratoluidine by arsenic acid (p. 621). In its properties and derivatives it is perfectly analogous to rosaniline. Its diazochloride,  $C_{19}H_{12}(OH)N_6Cl_3$ , yields *aurin*,  $C_{19}H_{14}O_3$ , when boiled with water.

In para rosaniline and in para-leucaniline the amide groups in the three benzene nuclei occupy the para-position (referred to the point of union of the methane carbon). We infer this from the synthetic methods (from paranitrobenzaldehyde) and from their relations to the amines and to para-dioxybenzophenone (p. 611) (*Ber.*, 14, 330). It is very probable that common rosaniline contains its amide-groups in the same position; as it is obtained by means of ortho-toluidine the methyl in it occupies the meta-position referred to the methane carbon. In the rosaniline salts, as in malachite green, we assume that an amide nitrogen has united with the methane carbon, forming a chromogen atomic group (*Ber.*, 12, 2350).

**Triamido-diphenyl-tolyl Methane, Leucaniline,  $C_{20}H_{21}N_3$**   $= (NH_2.C_6H_4)_2CH.C_6H_3(CH_3).NH_2$ , is obtained by the reduction of trinitro-diphenyl meta-tolyl methane (p. 615), and is obtained by digesting the fuchsine salts with ammonium sulphide, or zinc dust and hydrochloric acid. The alkalis throw it out from its salts as a white, flocculent precipitate, which separates from water in small crystals. It yields colorless crystalline salts with three equivalents of acid. By diazotizing and replacing the diazo-groups by hydrogen (best by dissolving in concentrated sulphuric acid, conducting nitrous acid into the same, and boiling with alcohol, p. 458), leucaniline is changed into diphenyl-meta-tolyl methane. Oxidizing agents convert it into rosaniline (its salts).

The oxidation of the leucanilines to rosanilines succeeds best when they are heated with a concentrated arsenic acid solution, or with metallic oxides to 130–140°, or by boiling the alcoholic solution with chloranil. Paraleucaniline and common leucaniline are also converted into coloring substances by heating them with some drops of hydrochloric acid upon a platinum foil. This behavior readily distinguishes the second from some isomerides (*Ann.*, 194, 284).

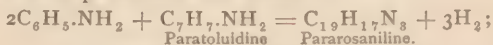
**Rosaniline,  $C_{20}H_{21}N_3O$ .** The rosaniline salts,  $C_{20}H_{19}N_3.HX$  (p. 618), are obtained in the oxidation of leucaniline, and are technically prepared by oxidizing a mixture of aniline and ortho- and para-toluidine (see below). Alkalies precipitate the *free base* (the carbinol),  $C_{20}H_{21}N_3O$ , from the salt solutions; it crystallizes from

alcohol and hot water in colorless needles or plates. It reddens on exposure, and when heated suffers decomposition. Its diazo-compounds, *e. g.*,  $C_{20}H_{14}(OH)N_6Cl_3$ , are produced when nitrous acid acts on the rosaniline salts, and when boiled with water they afford rosolic acid,  $C_{20}H_{16}O_3$ . Free rosaniline,  $C_{20}H_{21}N_3O$ , is a base, which will expel ammonia from the ammonium salts. It combines with one and three equivalents of acids, undergoing an anhydride formation (p. 617), and yields salts, *e. g.*,  $C_{20}H_{19}N_3 \cdot HCl$  and  $C_{20}H_{19}N_3 \cdot 3HCl$ . The latter are yellow-brown in color and not very stable; water decomposes them into the stable, mon-acidic salts with intense colors. These are applied as dyes. They are mostly readily soluble in water and alcohol, and crystallize readily in metallic, greenish crystals. Their solutions are carmine-red in color, and stain animal tissue directly violet-red, while vegetable fibre (cotton) must first be mordanted. The commercial *fuchsine* consists chiefly of the hydrochloride or acetate,  $C_{20}H_{19}N_3 \cdot C_2H_3O_2$ . The fatty-acid salts, insoluble in water and produced by dissolving the free rosaniline base in fatty acids, are employed in decorative printing.

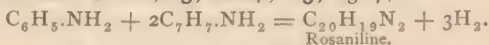
All the rosanilines are changed to colorless leucanilines when treated with reducing agents. When heated to  $200^\circ$  with hydrochloric or hydriodic acid, the rosanilines are broken up into their component anilines. Heated to  $200^\circ$  with water they yield ammonia, dioxybenzophenone and phenols.

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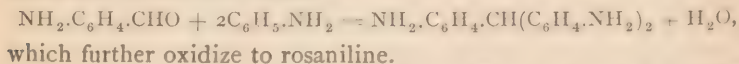
*Preparation.*—Technically the rosaniline salts are obtained by oxidizing aniline oil (a mixture of aniline with para- and orthotoluidine) with metallic salts (tin chloride, mercuric nitrate) or more advantageously with arsenic acid. If pure aniline be employed no coloring substance is formed. When pure aniline and paratoluidine are used pararosaniline results:—



whereas common rosaniline is obtained from aniline, paratoluidine and orthotoluidine (*Ber.*, 13, 2204; 15, 2367):—



The reaction probably occurs in such a manner that para-amido benzaldehyde is first produced from the paratoluidine, and this then (like para-nitrobenzaldehyde, p. 617) condenses with two aniline molecules to the leuco-bases:—

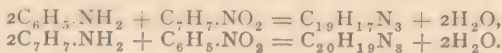


An interesting formation of pararosaniline is that of heating aniline with  $CCl_4$  to  $230^\circ$  when the latter affords the linking carbon

atom, and there ensues a reaction analogous to that of the formation of triphenyl methane from benzene and  $\text{CCl}_3\text{H}$  or  $\text{CCl}_4$  (p. 614).

In the preparation of rosaniline according to the *arsenic acid method* (Girard and Medloc) aniline oil, or better, the proper mixture of aniline and toluidine is heated during 7–10 hours with a concentrated arsenic acid ( $\frac{3}{4}$  part) solution in iron retorts with agitators until the mass assumes a metallic lustre. The product, consisting chiefly of rosaniline arsenite, is extracted with water and filtered. When the solution cools a violet dye-substance separates, and upon the addition of common salt rosaniline hydrochloride crystallizes out. The crystals thus obtained contain arsenic, but are freed from it by repeated crystallizations.

According to another method (by Coupier) applied technically, the oxidizing agent is either nitrobenzene or nitrotoluene, which is reduced and at the same time enters into the formation of the rosaniline:—

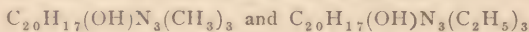


A mixture of aniline oil ( $\frac{2}{3}$  of this is applied in the shape of its  $\text{HCl}$ -salt) is heated to 180–190° with 50 per cent. nitrobenzene and 3–4 per cent. iron filings.

The commercial dye-stuffs, obtained as described, are really salts of rosaniline,  $\text{C}_{20}\text{H}_{19}\text{N}_3$ , and apparently contain, although in slight quantity, salts of pararosaniline,  $\text{C}_{19}\text{H}_{17}\text{N}_3$ , and the homologous base,  $\text{C}_{21}\text{H}_{21}\text{N}_3$ . The nitric acid salt,  $\text{C}_{20}\text{H}_{19}\text{N}_3\cdot\text{HNO}_3$ , called *Azalaïn*, was formerly prepared by oxidizing aniline oil with mercuric nitrate. The *fuchsine*, absolutely free of arsenic, which is obtained from it by a transposition with sodium chloride, is called *rubine*.

### Alkyl rosanilines.

When the rosaniline salts are heated with alkyl iodides or chlorides (and the alcohols) the hydrogen of the amido-groups can be replaced by alkyls. Of the trialkylic compounds:—



resulting in this manner, the methyl base affords reddish-violet-colored salts and the ethyl base pure violet salts (Hofmann's Violet, Dahlia); these are difficultly soluble in water, but dissolve easily in alcohol.

The introduction of more methyl affords higher methylated dyes. Hexamethyl-rosaniline is capable of uniting with  $\text{CH}_3\text{I}$  or  $\text{CH}_3\text{Cl}$  (1 molecule) to form *green* colored salts (see Methyl green, p. 622). The picrate, a dark green powder, and the crystalline  $\text{ZnCl}_2$ -double salt, readily soluble in water, constituted the *iodine green* or *night green* of commerce, but at present are supplanted by the cheaper methyl- and malachite-greens.

The phenylated rosanilines are obtained by heating rosaniline hydrochloride with aniline or toluidines (p. 432), or the free base with aniline and some benzoic acid. The triphenyl-rosaniline hydrochlorate,  $\text{C}_{20}\text{H}_{16}(\text{C}_6\text{H}_5)_3\text{N}_3\cdot\text{HCl}$ , appeared in commerce as



*aniline blue*, a bluish-brown crystalline powder with copper lustre, soluble in alcohol but not in water. To dissolve it in the latter sulpho-salts are prepared, which exhibit different shades of blue (*soluble blue*) corresponding to the number of sulpho-groups in them. At present diphenylamine blue and other dyes have taken its place. Diphenylamine results on distilling triphenyl-rosaniline.

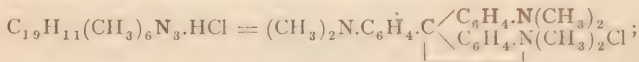
*Pararosaniline Derivatives.* Instead of first preparing rosaniline and then adding alkyl, it was suggested that the same compounds could be obtained by directly oxidizing alkyl anilines (dimethyl aniline, diphenylmethyl amine). The resulting dyes, according to their method of preparation, are derivatives of pararosaniline,  $C_{19}H_{17}N_3$ . They are probably produced as follows: A methyl group splits off and is oxidized to formic aldehyde, which then condenses three molecules of the alkyl anilines.

The following methyl derivatives have been obtained in a pure state:—

**Tetra-methyl Para-leucaniline**,  $H_2N.C_6H_4.CH \begin{smallmatrix} < C_6H_4.N(CH_3)_2 \\ < C_6H_4.N(CH_3)_2 \end{smallmatrix}$ , is obtained by reducing para-nitro leuco-malachite-green (p. 617), formed from para-nitrobenzaldehyde and dimethyl aniline. It melts at  $152^\circ$ . It is oxidized to **Tetramethyl Violet**,  $C_{19}H_{13}(CH_3)_4N_3.HCl$ . The acetate of paraleucaniline may be oxidized to a green dye (a malachite-green, as one  $NH_2$ -group is linked by acetyl (*Ber.*, 16, 708).

**Pentamethyl-para-leucaniline**,  $C_{19}H_{14}(CH_3)_5N_3$ , has been obtained from the reduction product of commercial methyl violet (a mixture of penta- and hexamethyl violet) by means of the acetate. It melts at  $116^\circ$ , and when oxidized yields **Penta-methyl Violet**,  $C_{19}H_{12}(CH_3)_5N_3.HCl$ . When its acetate is oxidized it yields a green dye (*Ber.*, 16, 2906).

**Hexamethyl-paraleucaniline**,  $C_{19}H_{13}(CH_3)_6N_3$ , is obtained pure on heating ortho-formic ester,  $CH(O.C_2H_5)_3$  with dimethyl aniline (3 molecules) and  $ZnCl_2$ , and from tetramethyl diamidobenzophenone (p. 611), with dimethyl aniline and  $PCl_3$ . If separated from its  $HCl$ -salt it crystallizes in silvery leaflets, and melts at  $173^\circ$ . If oxidized it yields **Hexamethyl Violet**:—



this possesses a blue tint. Its carbinol base,  $C_{19}H_{12}(OH)N_3(CH_3)_6$ , crystallized from ether, melts at  $190^\circ$ .

All three leucanilines yield the iodo-methylate,  $C_{19}H_{13}(CH_3)_6N_3.3CH_3I$ , when they are heated with much  $CH_3I$  and methyl alcohol. This melts at  $185^\circ$ , and heated to  $130^\circ$  regenerates hexamethyl-para-leucaniline.

Hexamethyl-paraleucaniline has the power of taking up one molecule of methyl chloride, bromide or iodide, with the formation of green colored salts—the *methyl greens* (see below).

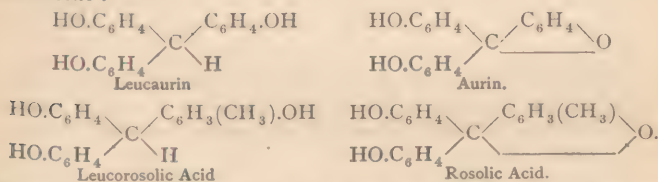
Commercial *methyl violet* (*Paris violet*) formed by the oxidation of dimethyl aniline (see above) with cupric salts (or chloranil) is a mixture of the hydrochlorides of penta- and hexa-methyl violet. It is a metallic green mass, dissolving in water and alcohol with a violet color. When methyl violet is heated with methyl nitrate or chloride we get the so-called *Methyl green* (see above), whose

HCl-salt,  $C_{19}H_{11}N_3 \cdot HCl \cdot CH_3Cl$ , appears as the  $ZnCl_2$ -double salt in the form of the golden green mass of the commercial dye. The blue *benzyl violets* are obtained by heating methyl violet with benzyl chloride.

Just as methyl violet is obtained from dimethylaniline, so can we prepare from diphenyl aniline, *e. g.*,  $(C_6H_5)_2N \cdot CH_3$  the so-called *diphenylamine blue*. The oxidizing agents are cupric nitrate,  $C_2Cl_6$  or oxalic acid. To render the blue dyes soluble in water they are converted into sulphonic acids; or we first prepare the sulpho-acids of the diphenylamines and then oxidize them. The sodium sulphates constitute the technical diphenylamine blues.

### PHENOL DERIVATIVES OF THE TRIPHENYL METHANES. AURINS.

These possess a constitution perfectly analogous to that of the amido-derivatives, as they contain hydroxyls in the positions held by the amido-groups. They are synthetically produced in a similar manner by the condensation of the phenols (p. 614), and on the other hand may be obtained from the amido-compounds by means of the diazo-derivatives. Their leuco-derivatives (p. 619), are oxidized to carbinols, which, however, are not stable, but immediately yield, by exit of water, colored anhydrides, called *aurins* or *rosolic acids*:—



**Dioxy-triphenyl Methane**,  $C_{19}H_{16}O_2 = C_6H_5 \cdot CH(C_6H_4.OH)_2$ , leucobenzaurin, is obtained from diamido-triphenyl methane (p. 616), with nitrous acid and by reducing benzaurin with zinc and hydrochloric acid. It crystallizes from dilute alcohol in yellow needles or prisms, melting at  $161^\circ$ . When oxidized it affords benzaurin.

**Dioxy-triphenyl Carbinol**,  $C_{19}H_{16}O_3 = C_6H_5 \cdot C(OH)(C_6H_4.OH)_2$ , is only stable as an *anhydride*,  $C_{19}H_{14}O_2$ , called *benzaurin*. The latter is produced in the condensation of phenotrichloride and phenol (similar to the formation of malachite-green):—



and from oxybenzophenone chloride (from oxybenzophenone, p. 611, with  $PCl_3$ ) and phenol:—

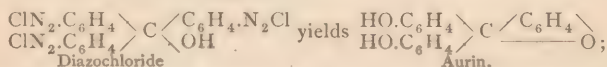


It is a metallic mass with a red lustre, dissolving in alcohol and ether with a yellow and in the alkalis with a red color. When fused with alkalis it decom-

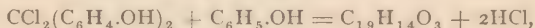
poses into benzene and dioxybenzophenone, which is further decomposed into paraoxybenzoic acid and phenol (p. 611).

**Trioxo-triphenyl Methane**,  $C_{19}H_{16}O_3 = CH(C_6H_4.OH)_3$ , **Leucaurin**. This is obtained in the reduction of aurin, its carbinol anhydride, by means of zinc dust. It dissolves in alcohol and acetic acid, and crystallizes in colorless needles, which become colored on exposure to the air. Oxidizing agents impart a deep red color to its solutions in the alkalis.

**Aurin**,  $C_{19}H_{14}O_3$ , is produced on boiling the diazo-hydrochloride of parosaniline with water, when the carbinol formed at first splits off water (*Ann.*, 194, 301):—



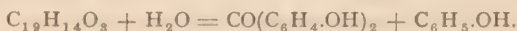
also by the condensation of dioxybenzophenone chloride (from dioxybenzophenone, p. 611) with phenol:—



and by the condensation of phenol with formic acid on heating with zinc chloride. It is made by heating phenol with oxalic and sulphuric acids; the combining carbon atom springs from the oxalic acid.

The method of Kolbe and Schmitt (1861) is that technically employed for the manufacture of aurin or yellow corallin. It consists in heating phenol (1 part and anhydrous oxalic acid ( $\frac{2}{3}$  part) with sulphuric acid ( $\frac{1}{2}$  part) to 130–150°. until the liberation of gas ceases (*Ann.*, 202, 185). On extracting with water there remains a resinous, metallic green mass which forms a yellow powder. It contains, besides aurin, various other, quite similar, substances, from which the first can be separated either by means of sulphurous acid (*Ann.*, 194, 123), or by precipitation as aurin-ammonia, when  $\text{NH}_3$  is conducted into the alcoholic solution (*Ann.*, 196, 177).

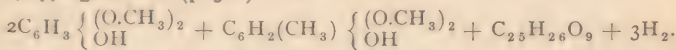
Aurin dissolves in hydrochloric acid, acetic acid and alcohol. It crystallizes in red needles or prisms with metallic lustre, melts at 220°, and yields phenol. Acids precipitate it from the alkaline fuchsine-red solutions. When ammonia is conducted into the alcoholic solution, the ammonium salt,  $\text{C}_{19}\text{H}_{11}(\text{NH}_4)\text{O}_3$ , separates in dark red needles with a steel-blue lustre. They give up ammonia on exposure to the air. The alkali salts are also unstable. With acids, however, aurin affords well crystallized compounds. With the primary alkaline sulphites it also yields colorless, crystalline derivatives, *e. g.*,  $\text{C}_{19}\text{H}_{14}\text{O}_3 \cdot \text{KHSO}_3$ . Digested with zinc dust and hydrochloric acid or acetic acid, it is reduced to leucaurin,  $\text{C}_{19}\text{H}_{16}\text{O}_3$ . Heated to 250° with water it breaks up into dioxybenzophenone and phenol:—



Aurin is changed to pararosaniline when it is heated with aqueous ammonia to 150°. An intermediate product (having 1 or 2 amide groups) is the so-called *Peonine* (red corallin). With aniline we obtain triphenyl-rosaniline, and the intermediate product is *Azuline*.

**Leuco-rosolic Acid**,  $C_{20}H_{18}O_3 = (HO.C_6H_4)_2.CH.C_6H_3(CH_3).OH$ , trioxy-diphenyl-tolyl methane, and **Rosolic Acid**,  $C_{20}H_{16}O_2$ , corresponding to leucoaniline and rosaniline are constituted similarly to leucaurin and aurin, and resemble them in all their reactions. Rosolic acid, like aurine, is obtained by boiling the diazo-chloride of rosaniline with water and by oxidizing a mixture of phenol and cresol,  $C_6H_4(CH_3)OH$ , with arsenic acid and sulphuric acid, whereby the linking methane carbon originates from the methyl group. When rosolic acid is digested with alcohol and zinc dust, it is reduced to leucorosolic acid.

The so-called *Pittical* belongs to the aurin series. It was first obtained in oxidizing the fractions of beech-wood tar, boiling at high temperatures. It consists of the dark blue salts of *Eupittonic acid* (Eupitton), which, in its uncombined state, shows an orange-yellow color. It can be synthesized, analogous to rosolic acid, by oxidizing a mixture of the dimethyl ester of pyrogallallic acid and methyl pyrogallallic acid (p. 501):—



Eupitton is, therefore, an aurin, into which six methoxyl groups have been introduced (comp. *Ber.*, 12, 1371):—

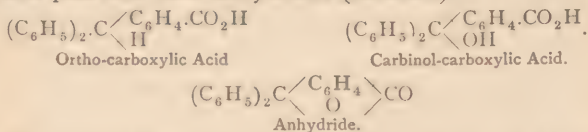


Eupitton forms orange-yellow crystals, melting with decomposition at 200°. It dissolves with a deep blue color in alkalis yielding salts, which are precipitated by excess of alkali. When heated with ammonia it suffers a replacement of its hydroxyls by amid-groups, just like aurin, and affords a body resembling rosaniline, which must be considered as hexamethoxyl rosaniline.

## CARBOXYL DERIVATIVES OF THE TRIPHENYL METHANES. PHTHALIDS.

Of the many possible carboxyl derivatives of the triphenyl methanes (their amido- and phenol derivatives), there is one group of compounds of particular interest. These contain a carboxyl in the benzene nucleus in the ortho position (in relation to the combining methane carbon.)\*

By oxidation they yield carbinol acids, which, however (like all  $\gamma$ -oxyacids), are not stable, but immediately sustain a loss of water and pass into their anhydrides (lactones):—

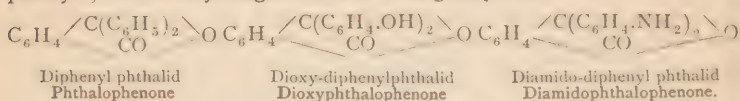


These anhydrides bear exactly the same relation to the carbinol-carboxylic acids as does the so-called *Phthalid* to the unstable

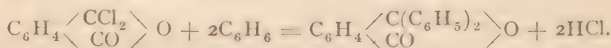
\* See further, A. Baeyer, *Ann.*, 202, 36, 212, 347.



ortho-oxy-methyl benzoic acid (p. 552). It is, therefore, convenient to regard the compounds belonging here as derivatives of phthalid, produced by the substitution of phenyls (oxy- and amido-phenyls) for the hydrogen of the  $\text{CH}_2$ -group:—



They are reduced to ortho-carboxylic acids, and may be obtained from phthalic acid in the same manner as phthalid, hence, their name. They are produced by the condensation of phthalic anhydride with phenols, on heating them with sulphuric acid (p. 627), and from phthalyl chloride (or phthalic anhydride) with benzenes, by the action of  $\text{AlCl}_3$ :—



In using phthalic anhydride, we first get orthobenzoyl benzoic acid (p. 613). On permitting benzene and  $\text{AlCl}_3$  to further act upon the latter, the product will be phthalophenone (*Ber.*, 14, 1865):—



Benzoyl benzoic acid reacts similarly with phenols (on heating to  $200^\circ$ ), and in this way phthalophenones can be obtained with one benzene and one phenol residue (*Ber.*, 14, 1859).

**Phthalophenone**,  $\text{C}_{20}\text{H}_{14}\text{O}_2$  (Diphenyl phthalid), the anhydride of triphenyl carbinol-ortho-carboxylic acid, is obtained from phthalyl chloride with benzene and  $\text{AlCl}_3$  (*Ann.*, 202, 50), or with mercury diphenyl (*Ber.*, 17, 387), and crystallizes from alcohol in leaflets, melting at  $115^\circ$ . When boiled with alkalis it dissolves to salts of triphenyl carbinol-ortho-carboxylic acid, which is again separated as anhydride (phthalophenone) by acids.

If the alkaline solution of the carbinol acid be boiled with zinc dust, we get **Triphenyl-methane-carboxylic Acid**,  $(\text{C}_6\text{H}_5)_2\text{CH.C}_6\text{H}_4\text{CO}_2\text{H}$ , melting at  $156^\circ$ , and when  $\text{CO}_2$  splits off it affords triphenyl methane.

Phthalophenone dissolves in nitric acid, yielding a dinitro-product, whose diamido-derivative is converted by nitrous acid into dioxyphthalophenone (phenol phthalein).

An interesting reaction is that triphenyl-methane carboxylic acid can, by the elimination of water, yield phenylanthranol, a derivative of anthracene:—



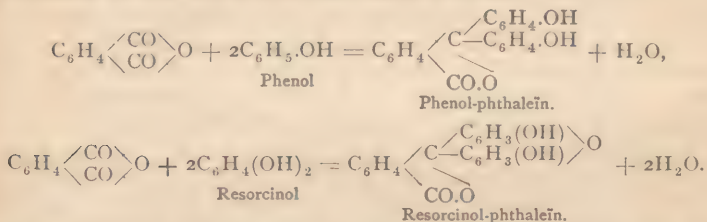
The derivatives of the acid deport themselves similarly (the so-called phthalins, p. 628); the resulting anthracene compounds are known as phthalidins (see these).

Just as phthalophenone is obtained from orthobenzoyl benzoic acid with benzene, we can get from phenol—

**Oxyphthalophenone**,  $C_{20}H_{13}(OH)O_2$ , Benzene-phenol-phthalid, melting at  $155^\circ$ . It forms the transition to the phthaleins, containing two phenol residues. It dissolves in alkalis with a violet-red color, which disappears on heating, because the anhydride group is ruptured and the salt of the carbinol acid produced; this by reduction with zinc dust yields

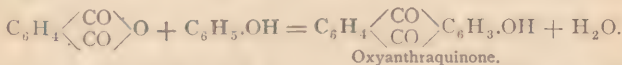
**Oxy-triphenyl-methane Carboxylic Acid**,  $C_6H_5 \cdot CH \begin{smallmatrix} \diagup C_6H_4 \cdot OH \\ \diagdown C_6H_4 \cdot CO_2H \end{smallmatrix}$ . This is a phthalin. Concentrated sulphuric acid abstracts water from it and converts it into its phthalidin (an anthracene derivative) (see above). Sulphuric acid decomposes oxyphthalophenone at  $100^\circ$  into phenol and ortho-benzoyl-benzoic acid. Fusion with potassium hydroxide converts it into benzoic acid and oxybenzophenone (p. 611).

The **Phthaleins**, the derivatives of phthalid containing two phenol residues, are particularly important, and are dyes which are of great technical value. A. Baeyer discovered them in 1871. They result from the condensation of phthalic anhydride (1 mol.) with phenols (2 mols.) on heating with sulphuric acid, or better, with  $ZnCl$  to  $120^\circ$  (or with oxalic acid, p. 614):—



The phthaleins derived from di- and polyvalent phenols are all anhydrides, formed by the elimination of water from two phenol-hydroxyls (*Ann.*, **212**, 347).

The reaction proceeds as in the case of phthalophenone (p. 626); we may assume that oxybenzoyl benzoic acid is first formed, and this then acts with a second molecule of the phenol. If, however, phthalic anhydride be heated to  $150^\circ$ , with but one molecule of phenol and sulphuric acid, we obtain anthraquinone derivatives:—

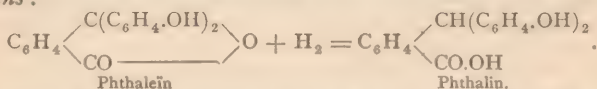


The free phthaleins are generally colorless, crystalline bodies. They dissolve in the alkalis with intense colorations, and are again separated from their solutions by acids (even  $CO_2$ ). The addition of concentrated caustic alkali causes the colors to disappear, because

by the rupture of the anhydride group we obtain salts of the colorless carbinol acids (p. 625). On diluting with water the colors reappear. The phthaleïns obtained from resorcinol and phthalic anhydride (or the anhydrides of polybasic fatty acids, p. 629) exhibit an intense fluorescence in their solutions, and are therefore termed *fluoresceïns*.

It appears the linking carbon atom (of phthalic acid) in them occupies the meta-position referred to the two hydroxyls of the resorcinol, and, therefore, only those meta-dioxybenzenes yield fluoresceïns in which the meta-position is unoccupied (*Ber.*, 15, 1375).

If the alkaline solutions of the phthaleïns be reduced with zinc dust, we obtain the non-coloring carboxylic acids (p. 626)—the *phthalins*:—



The phthaleïns may be compared to the amines, and the phthalins to the leucaurins (p. 624); in place of the hydroxyl of the latter the phthalins contain a carboxyl group. The hydroxyl, however, in the leucaurins is found in the para-position, while, in accordance with their method of production, the phthalins and phthaleïns contain the CO-group in the ortho-position.

The phthalins dissolve in alkalis, oxidize, however, readily in alkaline solution (even in the air, more quickly by  $\text{MnO}_2$  or  $\text{MnO}_4\text{K}$ ), to phthaleïns. Another interesting reaction is the conversion of the phthalins, by mixing them with sulphuric acid, into the so-called *phthalidins* (p. 627), which by oxidation yield the phthalideïns (oxanthranol derivatives) (see Anthranol).

**Phenol-phthaleïn**,  $\text{C}_{20}\text{H}_{14}\text{O}_4$ , Dioxynaphthalophenone, is also formed from phthalophenone when nitrous acid acts on the diamido-compound (p. 626). It is obtained on heating phthalic anhydride (3 parts) with phenol (4 parts) and tin chloride (4 parts), or with sulphuric acid to 115–120° for eight hours. The product is boiled with water, dissolved in sodium hydroxide and precipitated by acetic acid (*Ann.*, 202, 68). It is a yellow powder, crystallizing from alcohol in colorless crusts, and melting at 250°. It dissolves in the alkalis with a red color (see above). It is used as an indicator in alkalimetry, especially in determining  $\text{CO}_2$  with baryta (*Ber.*, 17, 1017, 1097).

Acetic anhydride converts it into a diacetate, melting at 143°, and bromine into a tetrabromide,  $\text{C}_{20}\text{H}_{10}\text{Br}_4\text{O}_4$ . On fusion with alkalis it decomposes into benzoic acid and dioxybenzophenone (p. 611). Boiling with alkaline hydroxides and zinc dust changes phthaleïn into **Phenol-phthalin**,  $\text{C}_{20}\text{H}_{16}\text{O}_4$ , crystallizing from hot water in needles, and melting at 225°. It dissolves in alkalis without coloration; the solution oxidizes to phenol-phthaleïn in the air, more quickly with potassium ferricyanide or  $\text{MnO}_4\text{K}$ .

**Resorcinol-phthaleïn**,  $\text{C}_{20}\text{H}_{12}\text{O}_5 + \text{H}_2\text{O}$ , **Fluoresceïn**, is prepared by heating phthalic anhydride (5 parts) with resorcinol (7 parts) to 200°. When precipitated from its salts it is a yellowish-red powder, and when crystallized ( $\text{C}_{20}\text{H}_{12}\text{O}_5$ ) from alcohol it is dark red in color. It decomposes about 290°. It dissolves in alcohol with a yellow-red color and green fluorescence. Its concentrated alkali solution is dark red, but on dilution it gradually becomes yellow,

and then exhibits a magnificent yellowish-green fluorescence. When fused with caustic soda it decomposes into resorcinol and mono-resorcinol phthalein, which further splits up into phthalic acid (benzoic acid) and resorcinol. **Resorcinol-phthalin, Fluorescein**,  $C_{20}H_{14}O_5$ , formed by the reduction with zinc dust, is a colorless, amorphous substance, which is again oxidized to fluorescein, when its alkaline solution is exposed to the air.

If bromine be allowed to act on fluorescein suspended in glacial acetic acid, we obtain substitution products, of which **Tetrabromfluorescein**,  $C_{20}H_8Br_4O_5$ , is the commercially important dye, **Eosin**. When thrown out of solution it is a yellowish-red precipitate; crystallized from alcohol it affords red crystals. The potassium salt,  $C_{20}H_6K_2Br_4O_5$ , containing 6 and 5 molecules of  $H_2O$ , is a red-brown powder with shining leaflets, and constitutes the eosin of commerce, soluble in water, and imparting to wool and silk a beautiful rose color (similar to cochineal). A benzyl derivative of fluorescein is the sodium salt of commercial *Chrysolin*, which dyes wool and silk directly, imparting to them a color resembling turmeric.

When pyrocatechin is gently warmed with phthalic anhydride and sulphuric acid, it yields a phthalein, which dissolves in caustic potash with a blue color and dyes like blue wood. Hydroquinone-phthalein dissolves in the alkalis with a violet color.

**Pyrogallol-phthalein, Gallein**,  $C_{20}H_{10}O_7$  (see *Ann.*, 209, 249), is obtained on heating pyrogallallic acid with phthalic anhydride to  $200^\circ$ . It dissolves with a dark red color in alcohol, and with a beautiful blue color in the alkalis. Zinc dust reduces it to *hydrogallein*,  $C_{20}H_{12}O_7$ , and then to *gallin*,  $C_{20}H_{14}O_7$ , which corresponds to phenol-phthalin.

Like all phthalins (p. 628), it is converted by sulphuric acid into the anthracene derivatives, *Coerulin*,  $C_{20}H_{12}O_6$ , and *Coerulein*,  $C_{20}H_8O_6$ . The latter dissolves in the alkalis with a green color, and finds application as a green dye.

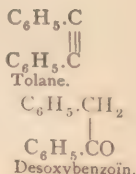
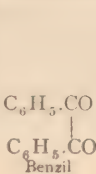
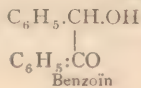
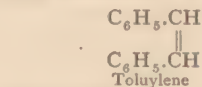
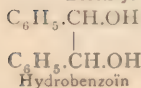
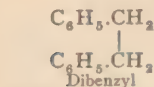
Phthalic anhydride also reacts with dimethylaniline, yielding

**Dimethylaniline-phthalein**,  $C_{24}H_{24}N_2O_2$ . With phthalyl chloride we get an isomeric body, the so-called *Phthal-green*, which is probably a phthalidin, and is derived from anthracene (*Ann.*, 206, 212).

The phenols can combine with the anhydrides of dibasic fatty acids (oxalic, succinic, maleic) and with tartaric acid, citric acid, etc. (*Ber.*, 15, 883), yielding analogous phthaleins and phthalins. **Succinyl fluorescein**,  $C_{16}H_{12}O_5$ , from succinic acid and resorcinol, yields a tetrabrom-derivative,  $C_{16}H_8Br_4O_5$ ; with bromine it yields a tetrabromide very similar to *Eosin*.

### 3. Derivatives with benzene nuclei joined by two or more carbon-atoms (p. 600).

#### 1. THE DIBENZYL GROUP.





**Dibenzyl**,  $C_{14}H_{14}$ , is prepared by the action of sodium or (copper) upon benzyl chloride,  $C_6H_5 \cdot CH_2Cl$ , or of  $AlCl_3$  upon benzene and ethylene chloride, and by heating stilbene and tolane, or benzoïn and desoxybenzoïn with hydriodic acid. It crystallizes in large prisms, melting at  $52^\circ$ , and boiling at  $284^\circ$ . Chromic acid and potassium permanganate oxidize it directly to benzoic acid. It yields two dinitro-compounds by nitration, the one melting at  $166^\circ$  (dipara), the other at  $74^\circ$ .

**Stilbene, Toluylene**,  $C_{14}H_{12} = C_6H_5 \cdot CH:CH \cdot C_6H_5$ , symmetrical diphenyl ethylene, is produced in various ways, thus: by distilling benzyl sulphide and disulphide; by the action of sodium upon bitter-almond oil or benzal chloride,  $C_6H_5 \cdot CHCl_2$ ; by conducting dibenzyl or toluene vapors over heated lead oxide; by heating diphenyl monochlorethane alone or diphenyl trichlorethane with zinc dust. It crystallizes in large monoclinic leaflets or prisms, dissolves easily in hot alcohol, melts at  $120^\circ$ , and distils at  $306^\circ$ . When heated with hydriodic acid it yields dibenzyl,  $C_{14}H_{14}$ . Chromic acid oxidizes it to bitter-almond oil and benzoic acid.

Bromine combines with stilbene, forming **Stilbene Dibromide**,  $C_6H_5 \cdot CHBr \cdot CHBr \cdot C_6H_5$ , dibromdibenzyl. It is also prepared from dibenzyl by the action of bromine and from the two hydrobenzoïns by means of  $PBr_5$ . It consists of silky needles, melting at  $237^\circ$ . Alcoholic potassium hydroxide converts it into **bromstilbene**,  $(C_6H_5)_2C_2HBr$  (melting at  $25^\circ$ ), and then into tolane.

With chlorine, stilbene (in chloroform solution) yields  **$\alpha$ -Stilbene Chloride**,  $(C_6H_5)_2C_2H_2Cl_2$ , which is also obtained from hydro- and isohydrobenzoïn with  $PCl_5$ . It melts at  $192^\circ$ .  **$\beta$ -Stilbene Chloride** is produced at the same time from hydrobenzoïn. It melts at  $93^\circ$ , and after heating to  $200^\circ$ , yields the  $\alpha$ -compound on crystallizing (*Ann.*, 198, 131).

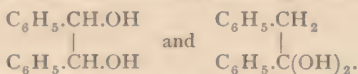
**Tolane**,  $C_{14}H_{10} = C_6H_5 \cdot C \equiv C \cdot C_6H_5$ , Diphenyl Acetylene, is produced from stilbene chloride on boiling with alcoholic potash. It is easily soluble in alcohol and ether, and consists of large crystals, melting at  $60^\circ$ . Chromic acid oxidizes it to benzoic acid.

Two **tolane dichlorides**,  $C_{14}H_{10}Cl_2$ , result on conducting chlorine into tolane (in chloroform solution). They can also be prepared by reducing tolane tetrachloride with iron and acetic acid (*Ber.*, 17, 1165); the  $\alpha$ - melts at  $143^\circ$ , the  $\beta$ - at  $63^\circ$ . Tolane also yields two **dibromides**,  $C_{14}H_{10}Br_2$ , with bromine, the  $\alpha$ -variety melting at  $208^\circ$ , the  $\beta$ - at  $64^\circ$ . Both regenerate tolane on treatment with alcoholic potash.

**Tolane Tetrachloride**,  $C_{14}H_{10}Cl_4$ , is produced from chlorobenzil (p. 632) with  $PCl_5$ , by chlorinating toluene (together with  $C_6H_5 \cdot CCl_3$ ) and by heating  $C_6H_5 \cdot CCl_3$  with copper. It affords brilliant crystals, which become porcelainous at  $100^\circ$  and melt at  $163^\circ$ . Heated with sulphuric acid to  $165^\circ$ , or glacial acetic acid to  $200^\circ$ , it yields benzil.

**Hydrobenzoïns**,  $C_{14}H_{10}O_2$ . Toluylene Glycols. Two isomeric bodies—hydrobenzoïn or isohydrobenzoïn—are produced when zinc and alcoholic hydrochloric acid act upon oil of almonds, or when the latter is treated with sodium amalgam. Both are also obtained from stilbene bromide or chloride, on converting the latter by silver acetate or benzoate into esters, and saponifying these with alcoholic ammonia. With potassium acetate, isohydrobenzoïn is almost the sole product. Hydrobenzoïn predominates (with a little isohydrobenzoïn) when sodium amalgam acts on benzil.

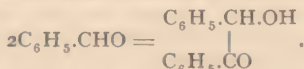
$PBr_3$  converts both into the same stilbene bromide (melting at  $237^\circ$ ); and with  $PCl_5$  both yield  $\alpha$ -stilbene chloride (the  $\beta$ -chloride is also produced from hydrobenzoïn). Chromic acid oxidizes both to bitter-almond oil and benzoic acid, but with nitric acid benzoïn and benzil are the products. All these reactions prove the two hydrobenzoïns to be but physical isomerides (see *Ann.*, 198, 191). The existence of two different aceto-esters and the analogy to the two dibenzyl dicarboxylic acids (p. 633), however, render it apparently possible that they are differently constituted chemically, according to the formulas—



*Hydrobenzoïn* is difficultly soluble in water, readily soluble in alcohol, crystallizes in large, shining, rhombic plates, melting at  $134^\circ$  and subliming without decomposition. The diacetate,  $C_{14}H_{12}(O.C_2H_3O)_2$ , is obtained from benzaldehyde and acetyl chloride by means of zinc dust; it consists of large prisms, melting at  $134^\circ$ .

*Isohydrobenzoïn* is more easily soluble in water than the preceding isomeride. It crystallizes in shining, four-sided prisms which contain water of crystallization, and rapidly effloresce on exposure. It crystallizes anhydrous from alcohol, and melts at  $119.5^\circ$ . Its diacetate is dimorphous, and crystallizes in shining leaflets, melting at  $118^\circ$ , or in rhombic prisms melting at  $106^\circ$ .

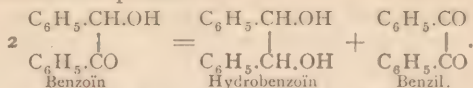
**Benzoïn**,  $C_{11}H_{12}O_2 = C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$ , a ketone alcohol, is produced when hydro- and isohydrobenzoïn are oxidized with concentrated nitric acid, and by the action of potassium cyanide upon benzaldehyde in alcoholic solution:—



All aromatic aldehydes afford the latter reaction; this is also true of furfural (p. 395). It is analogous to the condensation of the ketones to pinacones (p. 161) and to the conversion of aldehydes into alcohols and acids by alcoholic potash. The products are termed benzoïns, and are capable of reducing Fehling's solution, even at ordinary temperatures, when they are oxidized to benzils (diketones). All other ketone-alcohols possessing the group  $CO \cdot CH_2 \cdot OH$ , exhibit this property, though they are oxidized to oxy-acids (p. 214 and p. 510).

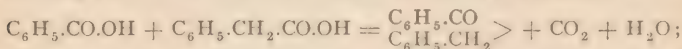
Benzoïn is difficultly soluble in water, cold alcohol and ether; it crystallizes in shining prisms, and melts at  $134^\circ$ . Nascent hydrogen converts it into hydrobenzoïn. When oxidized with chromic acid, it breaks up into benzaldehyde and benzoic acid. Hydro-

benzoïn and benzil (along with benzilic acid) are produced on boiling with alcoholic potash :—



Anisoïn, from anisic aldehyde, and cuminoïn, from cumin aldehyde, are very similar to benzoïn, and yield perfectly analogous derivatives (desoxybenzoïns, benzils and benzilic acids) (*Ber.*, 14, 323).

**Desoxybenzoïn**,  $\text{C}_{14}\text{H}_{12}\text{O} = \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ , phenyl-benzyl ketone, is obtained by reducing benzoïn or chlorobenzil,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CCl}_2\cdot\text{C}_6\text{H}_5$ , with zinc and hydrochloric acid; by heating monobromtoluylene with water to  $180\text{--}190^\circ$ ; by distilling a mixture of calcium benzoate and calcium phenyl-acetate :—



further, when  $\text{AlCl}_3$  acts upon a mixture of alphaltoluic chloride,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Cl}$  and benzene.

Homologous tolyl-benzyl ketone is formed in the same manner with toluene. Phenyl-benzyl ketone crystallizes from alcohol in large plates, melting at  $55^\circ$  and subliming undecomposed. It yields dibenzyl when heated with hydriodic acid. Sodium amalgam converts it into toluylene hydrate,  $\text{C}_{14}\text{H}_{14}\text{O} = \text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ , melting at  $62^\circ$  and decomposing, when boiled with dilute sulphuric acid, into toluylene and water; nitric acid again oxidizes it to desoxybenzoïn.

**Benzil**,  $\text{C}_{14}\text{H}_{10}\text{O}_2 = \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , Dibenzoyl, a diketone, is produced in the oxidation of benzoïn with nitric acid or chlorine; and by heating toluylene bromide with water and silver oxide (together with toluylene). It is insoluble in water, and crystallizes from alcohol and ether in large, six-sided prisms, melting at  $90^\circ$  and boiling at  $347^\circ$ . Chromic acid oxidizes it to benzoic acid, and nascent hydrogen reduces it to benzoïn. It yields an acetoxim with hydroxylamine— $\text{C}_6\text{H}_5\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , melting at  $131^\circ$ . Hydroxylamine-hydrochloride affords two *diphenyl-glyoxims*,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}_6\text{H}_5$  (p. 279); the  $\alpha$ . variety melts at  $237^\circ$  and the  $\beta$ . at  $206^\circ$  (*Ber.*, 16, 2177).

When benzil is allowed to stand for some time, with alcohols and some CNK, it sustains a decomposition into benzoic ester and benzaldehyde, which further changes to benzoic acid. Fural, but not isatin (*Ber.*, 16, 658), reacts similarly. When digested with  $\text{PCl}_5$  benzil yields chlorobenzil,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CCl}_2\cdot\text{C}_6\text{H}_5$ , melting at  $61^\circ$ . For the action of ammonia upon benzil, consult *Ber.*, 16, 690.

**Isobenzil**,  $\text{C}_{14}\text{H}_{10}\text{O}_2$ , is isomeric with the preceding, and is obtained from benzoyl chloride,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{Cl}$ , in alcoholic solution, by means of  $\text{NaHg}$ , and melts at  $156^\circ$  (*Ber.*, 16, 996).

On heating benzil with alcoholic potash or with water, above  $100^\circ$ , it changes to benzilic acid (p. 612) :—

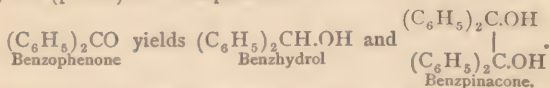


A transformation occurs here similar to that in the formation of the pinacolines from the pinacones (see below).

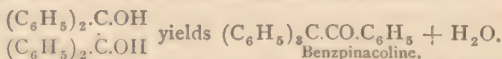
*Anisil*,  $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{C}_2\text{O}_2$ , from *anisoïn* and *cuminil*,  $(\text{C}_3\text{H}_7\cdot\text{C}_6\text{H}_4)_2\text{C}_2\text{O}_2$ , from *cuminoïn* (above), behave like benzil. When they are boiled or fused with caustic potash they afford *anisilic acid*,  $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$ , and *cuminilic acid*,  $(\text{C}_3\text{H}_7\cdot\text{C}_6\text{H}_4)_2\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$ .

## Pinacones and Pinacolines.

Nascent hydrogen, acting on the benzo-ketones, converts them, through a condensation of two molecules, into the pinacones (together with slight quantities of the secondary alcohols), which are also bivalent alcohols (glycols). In this behavior they resemble the ketones of the fatty series (p. 262). From benzophenone we get benzhydrol (p. 610) and benzpinacone :—



These pinacones, just like those of the fatty series, readily part with water (by heating with sulphuric or hydrochloric acid, or by the action of all reagents, which otherwise act upon hydroxyl—acetyl chloride, hydriodic acid and  $\text{PCl}_5$ ) and by an atomic rearrangement become pinacolone ketones :—



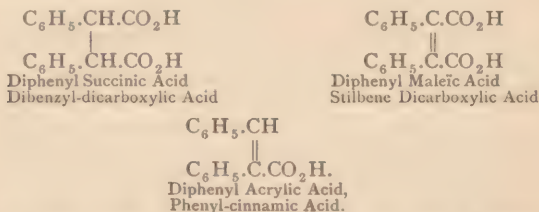
An analogous change occurs in the conversion of benzil into benzilic acid (see above), and of phenanthraquinone into diphenylene glycollic acid (p. 605). Therefore, the conception of the pinacone bodies may be further extended to all alcohols having two adjacent OH-groups (comp. *Annalen*, 198, 144).

**Benzpinacone**,  $\text{C}_{26}\text{H}_{22}\text{O}_2$ , formed from benzophenone by the action of zinc and sulphuric acid (*Ber.*, 14, 1402), crystallizes from alcohol in shining, small prisms, melting at  $185^\circ$  and splitting into benzophenone and benzhydrol. It sustains a like change when boiled with alcoholic potash.

On heating benzpinacone with hydrochloric or dilute sulphuric acid to  $200^\circ$ , by the action of methyl chloride upon it, or of zinc dust and acetyl chloride upon benzophenone, we get two

**Benzpinacolines**,  $\text{C}_{26}\text{H}_{20}\text{O}$ —the  $\alpha$ -, melting at  $205^\circ$ , the  $\beta$ -variety, at  $179^\circ$  (*Ber.*, 17, 912). Both decompose into triphenyl methane,  $(\text{C}_6\text{H}_5)_3\text{CH}$ , and benzoic acid on boiling with alcoholic potash.

## Carboxyl Derivatives :—



**Diphenyl-succinic Acid** ( $\alpha$ ),  $\text{C}_{16}\text{H}_{14}\text{O}_4$ , is produced on heating phenyl-bromacetic acid (p. 540) with alcoholic CNK :—



also (together with the  $\beta$ -acid), from the anhydride of stilbene dicarboxylic acid. The acid crystallizes from water in prisms, melting at  $183^\circ$ , and decomposing at the same time into water and its anhydride. When ignited with lime



it yields dibenzyl and stilbene. Heated to  $200^{\circ}$  with hydrochloric acid it changes to the  $\beta$ -acid. Its *anhydride*,  $C_{16}H_{12}O_3$ , obtained by fusing the  $\beta$ -acid, melts at  $220^{\circ}$ , and unites with water, re-forming the acid.

The isomeric  $\beta$ -Dibenzyl-dicarboxylic Acid is produced from the anhydride of stilbene dicarboxylic acid with sodium amalgam; and from dicyan stilbene,  $(C_6H_5)_2C_2(CN)_2$ , when heated with sodium amalgam or when heated with hydrochloric acid. It is insoluble in water and melts at  $229^{\circ}$ , when it yields water and the anhydride of the  $\alpha$ -acid. It suffers a like change into the  $\alpha$ -acid when heated with baryta water (comp. *Ber.*, 14, 1803).

**Stilbene Dicarboxylic Acid**,  $C_{16}H_{12}O_4$ , diphenyl maleic acid, if separated from its salts, at once decomposes into water and its anhydride. Its salts are made by boiling the nitrile with alcoholic potash. The *nitrile*,  $(C_6H_5)_2C_2(CN)_2$ , dicyanstilbene, is derived from phenyl-brom-acetic nitrile,  $C_6H_5.CHBr.CN$  (obtained from benzyl cyanide with bromine), on heating it alone or with alcoholic potassium cyanide. It melts at  $158^{\circ}$ . The anhydride of the acid,  $C_{16}H_{10}O_3$ , melts at  $151^{\circ}$  (*Ber.*, 14, 1797).

**Phenyl-cinnamic Acid**,  $C_{15}H_{12}O_2 = C_6H_5.CH:C(C_6H_5).CO_2H$ , is obtained by the condensation of benzaldehyde with sodium phenyl acetate,  $C_6H_5.CH_2.CO_2Na$  (see *Ber.*, 14, 924). It crystallizes from hot water in long needles, melting at  $170^{\circ}$  and then subliming.

**Tetraphenyl Ethane**,  $C_{26}H_{22} = (C_6H_5)_2CH.CH(C_6H_5)_2$ , is obtained from benzophenone by heating with zinc dust (along with diphenyl methane and tetraphenyl-ethylene); from benzpinacone and benzpinacoline with HI and phosphorus; from benzhydrol chloride,  $(C_6H_5)_2CHCl$ , by the action of zinc; from tetraphenyl ethylene by sodium and alcohol, etc. (*Ber.*, 17, 1039). It crystallizes from acetic acid or benzene in large prisms, melting at  $209^{\circ}$ .

**Tetraphenyl Ethylene**,  $C_{26}H_{20} = (C_6H_5)_2C:C(C_6H_5)_2$ , formed together with tetraphenyl ethane, from benzophenone, is also obtained on heating benzophenone chloride,  $(C_6H_5)_2CCl_2$ , with silver. It crystallizes from benzene in fine needles, melting at  $221^{\circ}$ . Both hydrocarbons are split into two molecules of benzophenone when oxidized.

Derivatives, containing two benzene nuclei linked by a chain of three carbon atoms, are:—

**Dibenzyl Ketone**,  $(C_6H_5.CH_2)_2CO$ , produced on distilling calcium alpha-toluate; it melts at  $30^{\circ}$  and boils at  $320^{\circ}$ . When reduced with hydriodic acid it forms **Dibenzyl methane**,  $(C_6H_5.CH_2)_2CH_2$ , boiling at  $290$ – $300^{\circ}$ .

**Dibenzoyl Methane**,  $(C_6H_5.CO)_2CH_2$ , is a di-ketone (p. 547).

**Dibenzyl Glycollic Acid**,  $C_{16}H_{16}O_3 = (C_6H_5.CH_2)_2C(OH).CO_2H$ , **Oxatolyl Acid**, is produced from dibenzyl ketone,  $(C_6H_5.CH_2)_2CO$ , by means of CNK and hydrochloric acid, and when vulpic and pulvic acids are boiled with dilute alkalis. It is almost insoluble in water, and crystallizes from alcohol in prisms, melting at  $156^{\circ}$ . When boiled with concentrated potassium hydroxide it decomposes into oxalic acid and two molecules of toluene (*Ann.*, 219, 41).

From diphenyl-diacetylene,  $C_6H_5.C:C:C.C_6H_5$  (p. 574), we get

**Dibenzoyl Succinic Acid**,  $C_{18}H_{14}O_6 = \begin{array}{c} C_6H_5.CO.CH.CO_2H \\ | \\ C_6H_5.CO.CH.CO_2H \end{array}$ , the diethyl

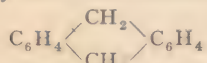
ester of which is obtained from sodium benzoyl acetic ester (p. 547) by the action of iodine, just as we form di-aceto-succinic ester (p. 222) from aceto-acetic ester. On boiling the ester with dilute sulphuric acid we get (by saponification and

elimination of water) the *mono-lactone*,  $C_{18}H_{12}O_5$  (corresponding to carbopyro-tritartaric acid), and di-lactone,  $C_{18}H_{10}O_4$ . These are closely related to *pulvic* and *vulpic* acids (*Ber.*, 17, 60).

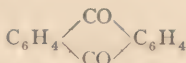
**Vulpic Acid**,  $C_{19}H_{14}O_5 = C_{18}H_{11}(CH_3)O_5$ , occurs in the lichen *Cetraria vulpina* and in a certain moss (12 per cent.), from which it may be extracted by chloroform or lime water. It is difficultly soluble in water and ether, crystallizes from alcohol in yellow prisms, melting at  $110^\circ$  and subliming. When boiled with lime water it is converted into methyl alcohol and *pulvic acid*,  $C_{18}H_{12}O_5$ . The latter melts at  $214^\circ$ , and when boiled with alkalis yields  $2CO_2$  and dibenzyl glycollic acid; oxalic acid and phenyl-acetic acid are produced on boiling with baryta water (*Ber.*, 14, 1686, *Ann.*, 219, 50).

## ANTHRACENE GROUP.

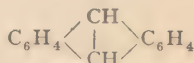
The members of this group contain two benzene nuclei, joined to each other by two doubly united carbon-atoms. In each benzene nucleus two ortho-positions are occupied. Therefore, we may designate them *Diortho-diphenylene Derivatives* (p. 604); usually, however, their names are derived from anthracene, from which they were first obtained:—



Diphenylene Dimethylene  
Hydranthracene



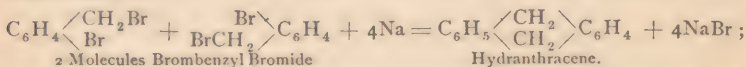
Diphenylene Diketone  
Anthraquinone



Anthracene.

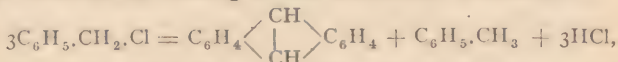
Hydranthracene passes readily into anthracene by the loss of 2 hydrogen-atoms; whereby we may suppose a mutual union of the two methane carbons takes place. Therefore, anthracene is mostly formed by its synthetic methods. Of the numerous syntheses of anthracene and diphenylene derivatives, analogous to those of the diphenyl methane derivatives (comp. p. 607), only such will be noticed, as are necessary for the establishment of the constitution of the compounds.

Hydranthracene is obtained from ortho-brom-benzyl bromide,  $C_6H_4Br.CH_2Br$ , by the action of sodium upon the ethereal solution; the bromine atoms of two molecules are withdrawn, and the residues combine:—

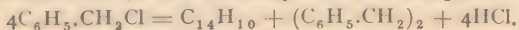


at the same time 2 hydrogen-atoms separate from the hydranthracene and large quantities of anthracene are produced.

Anthracene is likewise obtained (together with toluene) from benzyl chloride, on heating it with aluminium chloride:—

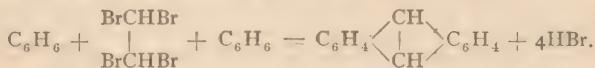


or with water to  $200^\circ$ , when dibenzyl will also be produced:—

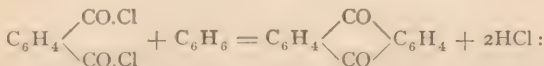


Anthracene (together with diphenyl methane) results also from the action of  $\text{AlCl}_3$  upon benzene and  $\text{CH}_2\text{Cl}_2$  (2 molecules).

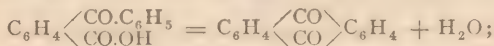
A noteworthy synthetic method is that from benzene and symmetrical tetrabrom-methane with  $\text{AlCl}_3$  :—



The formation of anthraquinone or diphenylene diketone from phthalic chloride and benzene, by heating with zinc dust to  $200^\circ$ , is very evident :—



likewise, that from ortho-benzoyl benzoic acid when the latter is heated with phosphoric anhydride :—

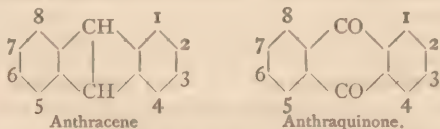


and by the distillation of calcium phthalate.

Again, when ortho tolyl-phenyl ketone,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ | \\ \text{CH}_3 \end{array} \text{C}_6\text{H}_5$  (p. 612), is heated with lead oxide, anthraquinone is produced. If zinc dust be employed anthracene results. In the same manner anthracene is formed from orthotolyl-phenyl methane,  $\text{C}_6\text{H}_4(\text{CH}_3).\text{CH}_2.\text{C}_6\text{H}_5$ , and methyl anthracene, etc., from orthoditolyl-methane,  $\text{C}_6\text{H}_4(\text{CH}_3).\text{CH}_2.\text{C}_6\text{H}_4.\text{CH}_3$ , etc.

It follows from all these syntheses (by means of ortho-derivatives of benzene), that in one of the benzene nuclei of anthracene and its derivatives, the two carbon-atoms are inserted in the ortho-position; that this is true, too, of the second nucleus is inferred from the production of anthracene and its hydride from orthobrom-benzyl bromide (p. 635); also from the behavior of oxanthraquinone,  $\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_3.\text{OH}$ , which is synthesized from brom-ortho-benzoyl benzoic acid,  $\text{C}_6\text{H}_5.\text{CO.C}_6\text{H}_3.\text{Br.CO}_2\text{H}$  (from brom-phthalic acid), and when oxidized (the second benzene nucleus being destroyed) yields phthalic acid,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$  (*Ber.*, 12, 2124).

Therefore, anthracene and its derivatives possess a symmetrical constitution, corresponding to the symbols :—



in which the numbers designate the eight affinities of the two benzene nuclei. The positions 1, 4, 5, 8 are alike, also 2, 3, 6, 7; the former (as with naphthalene, see this) are called the  $\alpha$ -, the latter the  $\beta$ -positions. We conclude, then, that if one hydrogen atom of the benzene ring be replaced two isomeric mono-derivatives ( $\alpha$  and  $\beta$ ) of anthracene and anthraquinone can be formed; whereas by the entrance of two similar substituting groups 10 isomeric di-derivatives result (p. 640). By the replacement of the middle hydrogen atoms of anthracene other isomerides are obtained, which have been termed  $\gamma$ -derivatives.

The two middle carbon atoms of anthracene form, with two carbon atoms from each of the two benzene nuclei, a closed chain consisting of six carbon atoms, resembling the ring of benzene. Hence anthracene is included among the condensed benzenes (see naphthalene). In most of the transformations of anthracene the intermediate carbon atoms are attacked first.

**Anthracene**,  $C_{14}H_{10}$ , is formed, in addition to the syntheses given, from many carbon compounds when they are exposed to a high heat, and for that reason it is produced in larger quantities in coal-tar.

Pure anthracene is obtained from the commercial product (boiling at  $340-360^\circ$ ) by crystallization from hot xylene and alcohol, or by extraction with acetic ester or  $CS_2$  (*Ann.*, **191**, 288). Or, hydranthranol is first obtained from anthraquinone (p. 638) and then boiled with water (*Journ. pract. Chemie*, **23**, 146).

Anthracene crystallizes in colorless monoclinic tables, showing beautiful blue fluorescence. It is difficultly soluble in alcohol and ether, but easily in hot benzene. It melts at  $213^\circ$ , and distils somewhat above  $360^\circ$ . Picric acid in benzene solution unites with it, yielding  $C_{14}H_{10} \cdot 2C_6H_3(NO_2)_3O$ , crystallizing in red needles, and melting at  $170^\circ$ .

When the cold saturated solution of anthracene in benzene is exposed to sunlight, a modification of anthracene, *Para-anthracene*,  $C_{14}H_{10}$ , separates out in plates. It is soluble with difficulty in benzene, is not attacked by nitric acid or bromine, melts at  $244^\circ$ , and in so doing reverts to common anthracene.

**Anthracene Dihydride**,  $C_{14}H_{12}$ , results from the action of sodium amalgam upon the alcoholic solution of anthracene, or on heating the latter or anthraquinone with hydriodic acid and phosphorus. It consists of monoclinic plates, readily soluble in alcohol, melting at  $107^\circ$ , and decomposing at  $305^\circ$ . It sublimes at low temperatures, in shining needles, and breaks up, at a dark red heat, into anthracene and hydrogen. It suffers the same change very easily when digested with concentrated sulphuric acid, the latter being reduced to  $SO_2$ . When anthracene or the dihydride is heated with hydriodic acid and amorphous phosphorus to  $220^\circ$  **Anthracene hexahydride**,  $C_{14}H_{16}$ , results. It is very soluble in alcohol and ether, crystallizes in leaflets, melts at  $63^\circ$ , boils at  $290^\circ$ , and at a red heat decomposes into anthracene and hydrogen.

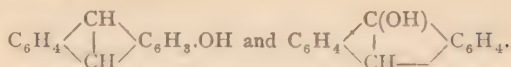
Mono- and di-halogen anthracenes are obtained when chlorine and bromine act upon anthracene (in  $CS_2$  solution). The two middle carbon atoms are substituted. **Nitroanthracene** could not be obtained. Nitric acid (concentrated and diluted, and also in alcoholic solution) oxidizes it to anthraquinone and dinitroanthraquinone.

**$\beta$ -Amido-anthracene**,  $C_{14}H_9 \cdot NH_2$ , called anthramine, is formed on heating  $\beta$ -anthrol (see below) with alcoholic  $NH_3$  to  $170^\circ$ . It affords yellow leaflets, melting at  $237^\circ$ .

When anthracene is dissolved in sulphuric acid two **Disulphonic Acids**,  $C_{14}H_8(SO_3H)_2$  ( $\alpha$  and  $\beta$ ), are produced. These, fused with caustic potash, yield two dioxy-anthracenes and also the corresponding dioxyanthraquinones.



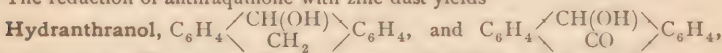
*Oxy-anthracenes*,  $C_{14}H_9.OH$ :—



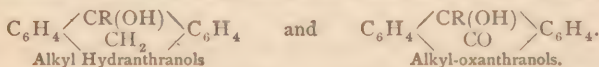
Two isomeric compounds ( $\alpha$  and  $\beta$ ) correspond to the first formula; they are phenols and are called *anthrols*.  $\beta$ -**Anthrol** has been obtained from anthracene-sulphonic acid (from  $\beta$ -anthraquinone sulphonic acid) and by the reduction of oxyanthraquinone. It crystallizes in leaflets, dissolving with a yellow color in the alkalis, and in sulphuric acid with a blue color when heated. After the introduction of the acetyl group in OH (compare oxidation of phenols, p. 494)  $CrO_3$  and acetic acid oxidize it to oxyanthraquinone.

**Anthranol** has the second formula; it is produced by the careful reduction of anthraquinone with hydriodic acid and phosphorus. It crystallizes from alcohol in shining needles, melting with decomposition at  $165^\circ$ . Chromic acid oxidizes it to anthraquinone.

The reduction of anthraquinone with zinc dust yields



**Oxanthranol**. These form *alkyl compounds* with KOH and the alkyllogens:—



The former, when boiled with hydrochloric acid, part with water and yield *alkyl anthracenes*,  $C_6H_4 \begin{array}{c} \diagup CR \\ | \\ CH \diagdown \end{array} C_6H_4$ ; the latter are also reduced to alkyl anthracenes by zinc dust, but with hydriodic acid to alkyl anthra-hydrides,  $C_6H_4 \begin{array}{c} \diagup CRH \\ | \\ CH_2 \diagdown \end{array} C_6H_4$ , etc (*Ann.*, 212, 65).

Derivatives of anthranol, in which the hydrogen of the CH-group is replaced by *phenyls*, are the so-called *phthalidins* and appear on mixing the triphenyl-carboxylic acids with sulphuric acid (p. 628). When oxidized they pass into phenyl-oxanthranols,  $C_6H_4 \begin{array}{c} \diagup CX(OH) \\ | \\ CO \diagdown \end{array} C_6H_4$  (the phthalideins) and yield phenyl anthracene (p. 643), if ignited with zinc dust. **Phenyl anthranol** resembles anthranol, and melts at  $141-144^\circ$ .

**Dioxyanthracenes**,  $C_{10}H_8(OH)_2$ . Of the ten possible isomeric diphenols (pp. 636 and 640), two with the formula,  $HO.C_6H_3.C_2H_2.C_6H_3.OH$ , have been derived from the two anthracene disulphonic acids by fusion with caustic potash. By oxidizing their acetates with  $CrO_3$  (see above), and saponifying, they afford the corresponding dioxyanthraquinones; the  $\beta$ -compound (called chrysazol) yields chrysazin, the  $\alpha$ -compound (rufol) anthrarufin (p. 642). A third (called *flavol*) is obtained from  $\beta$ -anthraquinone-disulphonic acid.

**Anthraquinone**,  $C_{14}H_8O_2 = C_6H_4.C_2O_2.C_6H_4$ , Diphenylene diketone (p. 635), is produced very readily in addition to the synthetic methods given by oxidizing anthracene, anthrahydride, dichlor- and dibrom-anthracene with nitric or chromic acid. We can obtain it by adding pulverized potassium bichromate to a hot glacial acetic acid

solution of anthracene (*Ann. Sup.*, 7, 285) or with less expense by oxidation with the theoretical amount of a chromic acid mixture.

Anthraquinone sublimes in yellow needles, melting at  $277^{\circ}$ , and is soluble in hot benzene and nitric acid. It is very stable, and is altered with difficulty by oxidizing agents. Sulphurous acid does not reduce it (unlike the true quinones, v. p. 502). It reverts to anthracene if heated to  $150^{\circ}$  with hydriodic acid, or with zinc dust and ammonia. When fused with potassium hydroxide (at  $250^{\circ}$ ), it decomposes into two molecules of benzoic acid; heated with soda-lime it yields benzene and a little diphenyl. It affords an acetoxim, by its union with one molecule of hydroxylamine.

When anthraquinone is digested with bromine at  $100^{\circ}$  it becomes **Dibrom-anthraquinone**,  $C_{14}H_6Br_2O_2$ , subliming in yellow needles. It is more easily obtained by oxidizing with nitric acid; dichloranthraquinone is similarly formed. It affords alizarin if heated to  $160^{\circ}$  with caustic potash. A **monobrom-anthraquinone** ( $\beta$ ) has been obtained from tribrom-anthracene by oxidation, and melts at  $187^{\circ}$ .

**Dinitroanthraquinone**,  $C_{14}H_6(NO_2)_2O_2$ , is formed (with anthraquinone) on digesting anthracene with dilute nitric acid (1 part with 3 parts water). It consists of yellow needles or leaflets, melting at  $280^{\circ}$ , and like picric acid manifests the property of forming crystalline combinations (Fritzsche's Reagent) with many hydrocarbons. The **mononitroquinone** is obtained when anthraquinone is boiled with concentrated nitric acid. It is a light yellow powder, melting at  $230^{\circ}$  (*Ber.*, 16, 363). Various dyes are obtained from it through the action of sulphuric acid (*Ber.*, 17, 891).

Heated to  $250$ – $260^{\circ}$  with concentrated sulphuric acid anthraquinone yields  $\beta$ -**Anthraquinone-mono-sulphonic acid**,  $C_{14}H_7O_2 \cdot SO_3H$ , which crystallizes from water in yellow leaflets; fused with potassium hydroxide it forms oxanthraquinone. Protracted heating with 4–5 parts sulphuric acid affords two **disulphonic acids**,  $C_{14}H_6O_2(SO_3H)_2$  ( $\alpha$  and  $\beta$ ). The first may be synthesized by heating ortho-benzoyl benzoic acid (p. 613), with fuming sulphuric acid. Fused with KOH it yields anthraflavic acid (2OH) and flavopurpurin (3OH), while the second furnishes isanthraflavic acid (2OH) and anthrapurpurin (3OH). Two isomeric **Anthraquinone-disulphonic Acids** ( $\gamma$  and  $\delta$ ) are obtained from the two anthracene-disulphonic acids by oxidation with nitric acid, and if fused with KOH yield chrysazin and anthrarufin; trioxyquinone is produced simultaneously, as oxychrysazin or oxyanthrarufin (p. 642).

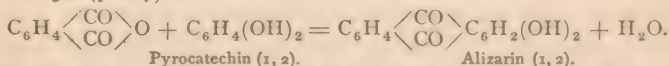
Anthraquinone is reduced, when digested with zinc dust and an alkaline hydroxide to,

**Anthrahydroquinone**,  $C_6H_4 \begin{array}{c} \diagup C(OH) \\ | \\ \diagdown C(OH) \end{array} C_6H_4$ , which is precipitated in yellow flakes by hydrochloric acid. If exposed to the air it again oxidizes to anthraquinone.

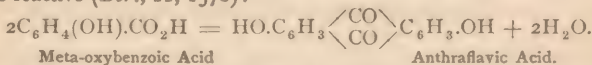
The **Oxyanthraquinones**, corresponding to the phenols, are derived by introducing hydroxyls into anthraquinone. There are two mono-oxy-anthraquinones,  $C_6H_4 \cdot C_2O_2 \cdot C_6H_3 \cdot OH$  ( $\alpha$  and  $\beta$ ) and ten dioxy-anthraquinones (p. 636), of which the latter are important as dyes. They originate from the brom (chlor) anthraquinones

and the sulphonic acids on fusion with alkalis, when the substituting groups are replaced by hydroxyls. By stronger fusion there generally ensues an additional entrance of hydroxyls (oxy- and dioxyanthraquinones result from the mono-sulphonic acid); the same is true in the fusion of the oxy-quinones—but, as it appears, this is only so for those derivatives which contain but one hydroxyl to each benzene nucleus (*Ber.*, **II**, 1613).

The oxyanthraquinones (like anthraquinone) may be synthetically prepared on heating phthalic anhydride with phenols (mono- and poly-valent) and sulphuric acid to 150° (p. 627):—



The di- and tetra-oxyquinones are also produced from the oxy- and dioxybenzoic acids, when heated with sulphuric acid, but it seems only the meta derivatives are reactive (*Ber.*, **II**, 1570):—



Continued fusion with alkalis causes the oxyanthraquinones to separate into their component oxybenzoic acids (same as anthraquinone decomposes into benzoic acid) and this reaction aids in the determination of the position of the isomerides (*Ber.*, **II**, 1293).

By heating the oxyanthraquinones with stannous chloride and sodium hydroxide, individual hydroxyls in them are reduced (*Ann.*, 183, 216). Heated to 150–160° with ammonia water single OH-groups are replaced by amide groups, which are further eliminated by diazotizing (*Ann.*, 183, 202). All anthraquinones are reduced to anthracene when heated with zinc dust.

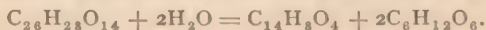
*Oxyanthraquinones*,  $\text{C}_{14}\text{H}_8\text{O}_3 = \text{C}_{14}\text{H}_7(\text{O}_2).\text{OH}.$

Ordinary **Oxyanthraquinone** ( $\beta$ ) is obtained from brom-anthraquinone and anthraquinone-sulphonic acid, and also from phthalic anhydride with phenol (together with erythro-oxyanthraquinone). It crystallizes in sulphur-yellow needles, melting at 302°, and sublimes in leaflets. Isomeric **erythro-oxyanthraquinone** ( $\alpha$ ) forms yellow needles, melting at 173–180°, and sublimes at 150°. Both oxyanthraquinones afford dioxyanthraquinone (alizarin), when fused with KOH.

*Dioxyanthraquinones*,  $\text{C}_{14}\text{H}_8\text{O}_4 = \text{C}_{14}\text{H}_6(\text{O}_2)(\text{OH})_2.$

Nine of the ten possible isomerides (p. 636), are known. Four of them contain the 2OH-groups in one and the same benzene nucleus; alizarin (from pyrocatechin) has the structure (1, 2), purpur-oxyanthin is (1, 3), quinizarin (from hydroquinone) is (1, 4); the fourth isomeride (2, 3) has not yet been discovered.

**1. Alizarin**, dioxyanthraquinone (1, 2), is the coloring ingredient of the root of the madder (*Rubia tinctorium*), in which it is contained as *ruberythric acid* (identical with morindin from *Morinda citrifolia*). Through the action of a ferment in the madder root, ruberythric acid decomposes when boiled with dilute acids or alkalis, or by standing with water, into glucose and alizarin:—



This decomposition into alizarin and glucose even takes place in the madder root when it is allowed to lie exposed to the air for some time. This was the basis for obtaining alizarin formerly, and for the application of madder root in dyeing. Later, different madder preparations were employed, in which the conversion into alizarin was more complete. Thus *garancin* was obtained by treating madder root with sulphuric acid, which decomposes the ruberythric acid, but does not alter the alizarin produced. At present artificial alizarin is employed almost exclusively.

Artificial alizarin was first obtained by Graebe and Liebermann, in 1868, when they heated dibrom-anthraquinone with potassium hydroxide. It is also produced from dichlor- and monobrom-anthraquinone, from the two oxy-anthraquinones and anthraquinone sulphonic acid, by fusion with caustic-potash at 250–270°. At present it is manufactured on a large scale by these methods. The fusion is dissolved in water, the alizarin precipitated by hydrochloric acid and purified by recrystallization or sublimation. Alizarin also results on heating phthalic anhydride with pyrocatechin and sulphuric acid (p. 640).

Alizarin crystallizes from alcohol in reddish-yellow prisms or needles, containing 3 molecules of  $H_2O$ , which escape at 100°. It melts at 282°, and sublimes in orange-red needles. It dissolves readily in alcohol and ether, and sparingly in hot water. In concentrated sulphuric acid it dissolves with a dark-red color and is precipitated by water unchanged. Its diacetate melts at 160°.

Alizarin is a diphenol, and like the substituted phenols behaves as an acid. It dissolves with a purple-red color in alkalis; lime and barium salts throw out the corresponding salts as blue precipitates. Alums and tin salts afford red precipitates (madder lakes); while ferric salts afford blackish-violet precipitates.

This property of alizarin yielding colored compounds with metallic oxides is the basis of its application in dyeing and cotton printing. The goods are mordanted with alumina (by immersing them in aluminium-acetate, then heating, whereby aluminium hydroxide is deposited on the fibres) and then dipped into the solution of alizarin; the resulting alizarin-aluminate is fixed by the fibres. In dyeing with turkey-red it is customary to mordant the goods with oil and alum.

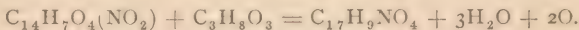
**Alizarin-amide**,  $C_{14}H_6O_2 \begin{smallmatrix} \diagup NH_2 \\ \diagdown OH \end{smallmatrix}$ , obtained by heating alizarin with water to 200°, crystallizes in needles, having metallic lustre, melts at 225° and sublimes. Heated with hydrochloric acid to 250° or by fusion with potassium hydroxide it yields alizarin; when diazotized it changes to oxyanthraquinone (p. 640).

**$\beta$ -Nitro-alizarin**,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H(NO_2)(OH)_2$  (1, 2, 3), *Alizarin-orange*, is produced by the action of vapors of hyponitric acid ( $NO_2$ ) acting on alizarin, or of nitric acid upon the glacial acetic acid solution (*Ber.*, 12, 584). It crystallizes from chloroform in orange-red leaflets with green reflex, and melts at 244°.

It yields phthalic acid when oxidized with nitric acid. Isomeric  $\alpha$  nitro-alizarin (1, 2, 4) is obtained by the nitration of diaceto-alizarin, it melts at 195°, and passes readily into purpurin.



When (1, 2, 3)-nitro-alizarin is heated with glycerol and sulphuric acid to  $100^{\circ}$  we obtain *alizarin-blue*,  $C_{17}H_9NO_4$  :—



The same occurs in trade in the form of a bluish-violet paste, and like alizarin is applied in dyeing. Since reducing agents decolorize it (zinc dust, grape sugar) and it again separates on exposure to the air, it is adapted to the vat-dyeing. It combines with 2 molecules  $NaHSO_3$ , yielding a compound soluble in water (same as quinoline)—the so-called *soluble alizarin-blue*.

Alizarin-blue crystallizes from benzene in metallic, brown-violet needles, which melt at  $270^{\circ}$  and sublime. Heated with zinc dust it affords anthraquinolin,  $C_{17}H_{11}N$  (see this); it is, therefore, a derivative of the latter, and is similarly obtained from nitroalizarin and glycerol, just as quinoline is derived from nitrobenzene and glycerol.

Of the alizarin isomerides (p. 640), *quinizarin* (1, 4), *purpuroxanthin* (1, 3), and *frangulinic acid*, (from the glucoside frangulin) contain both hydroxyls in one benzene nucleus—whereas *anthraflavic acid*, *iso-anthraflavic acid*, *metabenz-dioxyanthraquinone* (from m-oxybenzoic acid, p. 640), *anthrarufin* and *chrysazin* have the two hydroxyls in the two benzene nuclei.

Chrysazin is obtained from its tetranitro-compound,  $C_{14}H_2(NO_2)_4(O_2)(OH)_2$ , the so-called *chrysammic acid*, by reduction and the replacement of the amid-groups. This latter acid is obtained on digesting aloës with concentrated nitric acid.

**Trioxyanthraquinones**,  $C_{14}H_5O_2(OH)_3$ .

These are produced on oxidizing dioxyanthraquinones or upon fusing them with alkalis (p. 640).

1. **Purpurin**,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H(OH)_3$  (1, 2, 4), is present with alizarin in the madder root, and is separated from it by a boiling alum solution, which does not dissolve the latter. It is prepared artificially by heating alizarin and quinizarin with  $MnO_2$  and sulphuric acid to  $150^{\circ}$ ; purpuroxanthin is oxidized to purpurin by simply exposing its alkaline solution to the air. It is also obtained from tribrom-anthraquinone. Purpurin crystallizes with one molecule of  $H_2O$ , in reddish-yellow needles or prisms, which, at  $100^{\circ}$ , lose water and then sublime. It dissolves with a pure red color in hot water, alcohol, ether and the alkalis. Lime and baryta water yield purple-red precipitates. Goods previously acted on by mordants are dyed the same as by alizarin. It oxidizes to phthalic and oxalic acids when boiled with nitric acid; it yields anthracene upon distillation with zinc dust. Its triacetate melts at  $190$ – $193^{\circ}$ .

*Purpurin-amide*,  $C_{14}H_5O_2(OH)_2NH_2$  (see alizarin amide, p. 641), is obtained on digesting purpurin with aqueous ammonia at  $150^{\circ}$ ; it crystallizes in brownish-green needles, with metallic lustre, and passes into purpuroxanthin by the replacement of the amido-group by hydrogen.

**Flavopurpurin**, **anthra-purpurin** and **oxy-chrysazin** are isomerides of purpurin.

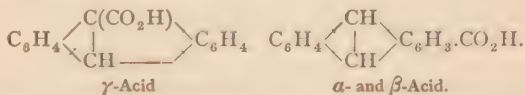
Its tetraoxyanthraquinones,  $C_6H_2(OH)_2.(C_2O_2)_2.C_6H_2(OH)_2$ , are the so-called **anthrachrysone**, obtained by heating symmetrical dioxybenzoic acid with sulphuric acid (p. 640), and **rufiopin**,  $C_{14}H_8O_6$ , obtained from opianic acid (p.



the root of rhubarb. If distilled with zinc dust it affords methyl-anthracene. It consists of orange-red crystals, melting at 245–250°.

**Dimethyl-anthracene**,  $C_{14}H_8(CH_3)_2$ , has been obtained from the portions of aniline oil boiling at high temperatures. It consists of shining leaflets, melting at 224–225°. If oxidized it yields a quinone and a mono- and dicarboxylic acid. Isomeric **dimethyl anthracenes** have been obtained from xylyl chloride,  $C_6H_4(CH_3).CH_2Cl$ , on heating it with water (melting at 200°), from toluene and  $CH_2Cl_2$  with  $AlCl_3$  (B. P. 225°) and from ethylidene chloride,  $CH_3.CHCl_2$ , and benzene with  $AlCl_3$ . The latter contains the two methyl groups linked to the two intermediate carbon atoms, and melts at 179°.

**Anthracene Carboxylic Acids** :—



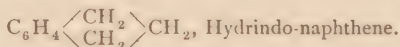
**$\gamma$ -Anthracene Carboxylic Acid** (its chloride) is formed when anthracene is heated with  $COCl_2$  to 200°. It is difficultly soluble in hot water, readily in alcohol, crystallizes in yellowish needles, and melts at 206°, with decomposition into  $CO_2$  and anthracene. Chromic acid in acetic acid solution oxidizes it to anthraquinone.

The  $\alpha$ - and  $\beta$ -acids are formed from the anthracene-mono-sulphonic acids by means of the cyanides, and from the anthraquinone carboxylic acids by reduction with ammonia and zinc dust; the  $\alpha$ -acid melts at 260°, the  $\beta$  acid at 280°.

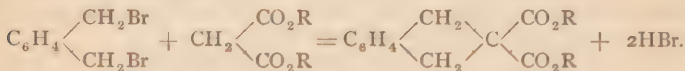
The **anthraquinone carboxylic acids**,  $C_6H_4(C_2O_2)C_6H_3.CO_2H$ , are produced by oxidizing the  $\alpha$ - and  $\beta$  carboxylic acids and methyl-anthraquinone with chromic acid in acetic acid. Both melt at 285°.

**Pseudo-purpurin**,  $C_{15}H_8O_7 = C_{14}H_4O_2(OH)_3.CO_2H$ , purpurin carboxylic acid, occurs in crude purpurin (from madder), and crystallizes from chloroform in red leaflets, melting at 218–220°. Further heating to 180° or boiling with  $KOH$  decomposes it into  $CO_2$  and purpurin.

**Hydrindo-naphthene**,  $C_9H_{10}$ , may be considered the transition member from benzene to naphthalene. It contains two benzene rings of six members. In it the benzene ring is combined with three carbon atoms, which form a closed chain, consisting of five members, with two carbon atoms. At present hydrindo-naphthene is only known in its carboxyl derivatives.



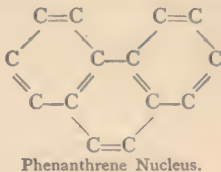
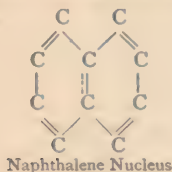
This ring-formation ensues, analogous to that of the tri- and tetra-methylene derivatives (p. 393), by the action of *o*-xylylene bromide (p. 415) upon malonic ester and sodium alcoholate :—



The resulting ether is saponified, and we then obtain **Hydrindo naphthene Dicarboxylic Acid**,  $C_9H_8(CO_2H)_2$ , melting at 199°, and decomposing into  $CO_2$  and **hydrindo-naphthene-mono-carboxylic acid**,  $C_9H_9.CO_2H$ , which melts at 130°, and distils without decomposition (*Ber.*, 17, 125).

## 4. DERIVATIVES WITH CONDENSED BENZENE NUCLEI.

The hydrocarbons belonging here contain two or more benzene nuclei so combined that every two nuclei have two adjoining carbon atoms in common, as seen in the following structural formulas of the nuclei of naphthalene,  $C_{10}H_8$ , and phenanthrene,  $C_{14}H_{10}$  :—



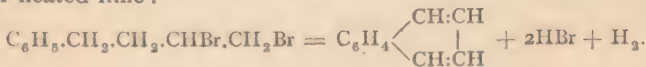
Phenanthrene, with three benzene rings, can also be considered as a diphenyl,  $C_6H_5-C_6H_5$ , in which two carbon atoms  $C=C$  in union with each other are inserted in the two ortho-positions of the two benzene nuclei, in such a manner that a third benzene ring is the result.

*Pyrene*,  $C_{16}H_{10}$ , *Chrysene*,  $C_{18}H_{12}$ , *Picene*,  $C_{22}H_{14}$ , also acenaphthene,  $C_{14}H_{10}$ , fluoranthene,  $C_{15}H_{10}$ , and other hydrocarbons have a similar structure; they are all found in those portions of coal-tar which boil at high temperatures.

## NAPHTHALENE.

**Naphthalene**,  $C_{10}H_8$ . This, like many other benzene hydrocarbons, is produced by the action of intense heat upon many carbon compounds, especially if they be conducted, in form of vapor, through tubes raised to a red heat. It is, therefore, present in coal-tar and separates as a brown mass from the portion boiling at  $180-200^\circ$ , when it cools. It is purified by distillation with water and by sublimation.

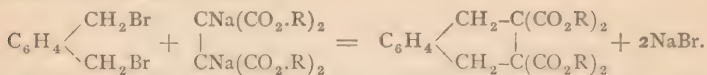
Naphthalene is synthetically prepared from phenyl butylene,  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH:CH_2$ , and its dibromide on leading the vapors over heated lime :—



Dihydro-naphthoic acid,  $C_{10}H_7(H_2) \cdot CO_2H$ , is formed in the same manner by heating benzyl acetoacetic ester,  $C_6H_5 \cdot CH_2 \cdot CH \begin{array}{c} \text{CO}_2H \\ \text{CO} \cdot CH_3 \end{array}$ , with sulphuric acid (with elimination of water). This parts with  $CO_2$ , and yields naphthalene hydride  $C_{10}H_8(H_2)$ —(*Ber.*, 16, 516). In both instances the side-chain, with 4 carbon-atoms, closes up, forming a benzene ring. A direct synthesis of the benzene ring of six members also ensues in a manner analogous to the formation of the trimethylene and tetramethylene ring (p. 393), and of hydrindo-naphthene



(p. 644, when o-xylylene bromide (p. 415) acts upon disodium-acetylene-tetracarboxylic ester (p. 374):—



First, we get the ester of tetrahydro-naphthalene-tetracarboxylic acid, and this by saponification yields tetrahydro-naphthalene dicarboxylic acid. Naphthalene results from the distillation of its silver salt (*Ber.*, 17, 448).

What is further noteworthy is the formation of  $\alpha$ -naphthol from isophenyl-crotonic acid (p. 581), by its elimination of water when boiled (*Ber.*, 16, 43:—

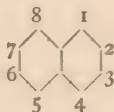


Naphthalene is difficultly soluble in cold alcohol, readily in hot alcohol and in ether. It crystallizes and sublimes in shining leaves, melting at  $79^\circ$ , and boiling at  $218^\circ$ . It is very easily volatilized, distils with aqueous vapor and possesses a peculiar odor. It affords a crystalline compound,  $\text{C}_{10}\text{H}_8\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$ , with picric acid; it crystallizes from alcohol in needles, melting at  $149^\circ$ . When boiled with dilute nitric acid it is oxidized to phthalic acid. Chromic acid slowly destroys it (p. 565).

Like the benzenes, naphthalene affords hydrogen and chlorine addition products. The hydrides (di- to deca-hydride) result on heating with  $\text{PH}_4\text{I}$ , or with hydriodic acid and phosphorus. The tetra-hydride,  $\text{C}_{10}\text{H}_8(\text{H}_4)$ , is a liquid with a penetrating odor, and boils at  $205^\circ$  (*Ber.*, 16, 3028). At a red heat the hydrides decompose into hydrogen and naphthalene.

If chlorine gas be conducted into naphthalene it melts and yields chlorine addition products. The *dichloride*,  $\text{C}_{10}\text{H}_8\text{Cl}_2$ , is liquid, and decomposes easily into monochloronaphthalene and  $\text{HCl}$ . The *tetrachloride*,  $\text{C}_{10}\text{H}_8\text{Cl}_4$ , crystallizes from  $\text{CHCl}_3$  in large rhombohedra, and melts at  $182^\circ$ . It decomposes into dichloronaphthalene,  $\text{C}_{10}\text{H}_6\text{Cl}_2$ , and  $2\text{HCl}$  when boiled, or by means of alcoholic potash.

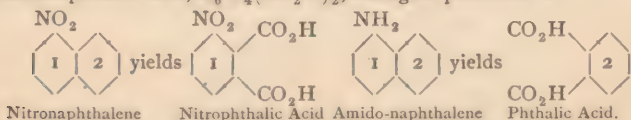
Naphthalene consists of two symmetrically condensed benzene nuclei (p. 645) (Erlenmeyer and Graebe) and its structure may be expressed by the symbol



in which the numbers indicate the eight affinities of the two benzene nuclei. According to this representation the positions 1, 4, 5 and 8 are alike, and so are 2, 3, 6 and 7 (same as in anthracene and anthraquinone, p. 636); the former are termed the  $\alpha$ -positions, the latter the  $\beta$ . It follows, that by the replacement of hydrogen

in naphthalene two series of isomeric mono-derivatives,  $C_{10}H_7X$  ( $\alpha$  and  $\beta$ ) can be derived, and with the di-derivatives,  $C_{10}H_6X_2$ , there are altogether ten isomerides possible.

These inferences relative to the number of isomerides and the accepted structure of the naphthalene nucleus are fully demonstrated by numerous reactions. The presence of a benzene ring in naphthalene follows from its syntheses and from its oxidation to phthalic acid,  $C_6H_4(CO_2H)_2$ , in which the 2 carbon-atoms of the carboxyl groups occupy the ortho-position. That there is a second benzene ring is shown by the fact that in the destruction of the first ring (by oxidations) phthalic acid or its derivatives are formed. Thus, by destroying the one ring we obtain nitro-phthalic acid,  $C_6H_3(NO_2)(CO_2H)_2$ , from nitro-naphthalene  $C_{10}H_7(NO_2)$ ; if, however, we reduce nitronaphthalene to its amide and oxidize the latter, the benzene ring containing the amido-group will be obliterated and a benzene derivative—phthalic acid,  $C_6H_4(CO_2H)_2$ ,—is again produced:—



The oxidation of the chlorinated naphthalenes led to perfectly analogous results (Graebe, *Ann.*, 149, 20).

The existence of two isomeric series of naphthalene mono-derivatives,  $C_{10}H_7X$ , indicates the presence of the two different positions ( $\alpha$  and  $\beta$ ). Atterberg afforded (*Ber.*, 9, 1736 and 10, 547) a direct proof that there are four  $\alpha$ -positions in naphthalene (two in each benzene nucleus).

That the  $\alpha$ -positions correspond to 1 (= 4, 5, 8) follows, as the  $\alpha$ -derivatives alone are capable of yielding a true quinone ( $\alpha$ -naphthoquinone) (Liebermann, *Ann.*, 163, 225). Nölting and Reverdin succeeded in showing that the  $\alpha$ -positions were contiguous to the two carbon atoms held in common by both benzene nuclei (*Ber.*, 13, 36). An evidence of this is the formation of  $\alpha$ -naphthol from isophenyl crotonic acid (p. 581).

Only the most important of the immense number of naphthalene derivatives will be mentioned in this connection. Reverdin and Nölting have prepared a monograph on these compounds, entitled, "Ueber die Constitution des Naphtalins," 1880.

### Halogen Derivatives.

**$\alpha$ -Chlor-naphthalene**,  $C_{10}H_7Cl$ , is produced in chlorinating boiling naphthalene; from naphthalene dichloride (p. 646) by means of alcoholic potash; from  $\alpha$ -naphthalene sulphonic acid with  $PCl_5$ , and from  $\alpha$ -amido-naphthalene by means of nitrous acid. It is a liquid, boiling about  $263^\circ$ .  **$\beta$ -Chlor-naphthalene**, from  $\beta$ -naphthol and  $\beta$ -naphthylamine, forms pearly leaflets, melts at  $56^\circ$ , and boils at  $265^\circ$ . **Perchlor-naphthalene**,  $C_{10}Cl_8$ , the final chlorination product, melts about  $203^\circ$ , and boils near  $400^\circ$ .

**$\alpha$ -Brom naphthalene**,  $C_{10}H_7Br$ , is produced by bromination; it is a liquid, and boils at  $277^\circ$ .  **$\beta$ -Brom-naphthalene**, from  $\beta$ -naphthylamine and  $\beta$ -naphthol, consists of brilliant leaflets, melting at  $57^\circ$  ( $68^\circ$ ).

**$\alpha$ -Iodo-naphthalene**,  $C_{10}H_7I$ , produced by action of iodine upon naphthyl mercury, solidifies only on cooling, and boils about  $300^\circ$ .  **$\beta$ -Iodo-naphthalene**, from  $\beta$ -naphthylamine, melts at  $54^\circ$ .

Homologous naphthalenes result from the two brom-naphthalenes by the action of alkylogens and sodium (p. 411), or more easily from naphthalene and alkyl bromides assisted by  $\text{AlCl}_3$ .

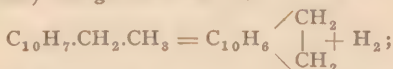
The methylated naphthalenes occur in coal-tar.

**$\alpha$ -Methyl-naphthalene**,  $\text{C}_{10}\text{H}_7\cdot\text{CH}_3$ , from  $\alpha$ -brom-naphthalene and  $\alpha$ -naphthyl-acetic acid (p. 654), is liquid, and boils at  $240\text{--}242^\circ$ .  **$\beta$ -Methyl-naphthalene**, from coal-tar, melts at  $32^\circ$ , and boils at  $242^\circ$  (*Ber.*, 17, 842).

**Dimethyl-naphthalene**,  $\text{C}_{10}\text{H}_6(\text{CH}_3)_2$ , from dibromnaphthalene and coal-tar, boils at  $251^\circ$ .

**$\alpha$ -Ethyl-naphthalene**,  $\text{C}_{10}\text{H}_7\cdot\text{C}_2\text{H}_5$ , from  $\alpha$ -brom-naphthalene, boils near  $259^\circ$ .  **$\beta$ -Ethyl-naphthalene**, from  $\beta$ -brom-naphthalene, boils about  $250^\circ$  (*Ber.*, 17, 1179).

**Acenaphthene**,  $\text{C}_{12}\text{H}_{10}$ , is obtained by conducting  $\alpha$ -ethyl naphthalene (or benzene and ethylene) through a red hot tube:—



this is similar to the formation of naphthalene from phenyl butylene (p. 645) Acenaphthene occurs in coal-tar, and it separates on cooling from the fraction boiling at  $265\text{--}275^\circ$ . It crystallizes from hot alcohol in long needles, melting at  $95^\circ$ , and boiling at  $277^\circ$ . Chromic acid oxidizes it to naphthalic acid,  $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ . It unites with picric acid to form long red needles of  $\text{C}_{12}\text{H}_{10}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$ , melting at  $161^\circ$ . If the vapors of acenaphthene be passed over ignited plumbic oxide, two hydrogen atoms split off and there results

**Acetylene Naphthalene**,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \diagup \text{CH} \\ || \\ \diagdown \text{CH} \end{array}$ , crystallizing from alcohol in yellow

plates, subliming even at the ordinary temperatures, melting at  $92^\circ$ , and boiling with partial decomposition at  $270^\circ$ . Its picric acid derivative melts at  $202^\circ$ . Chromic acid oxidizes it to naphthalic acid.

**Nitroso-naphthalene**,  $\text{C}_{10}\text{H}_7(\text{NO})$ , results from the action of nitrosyl bromide upon mercury dinaphthyl in  $\text{CS}_2$  solution. Ligroïne throws it out of its benzene solution in yellow warts, which redden on exposure. It melts at  $89^\circ$ , decomposes at  $134^\circ$ , possesses a pungent odor, and is readily volatilized in aqueous vapor. It dissolves in sulphuric acid with a cherry-red color. Sulphuric acid imparts a deep-blue color to its solution in phenol (comp. p. 430).

**Nitro-naphthalene**,  $\text{C}_{10}\text{H}_7(\text{NO}_2)$ . At present only the  $\alpha$ -derivative is known; this is produced in the nitration of naphthalene.

*Preparation.*—Dissolve naphthalene in glacial acetic acid, add nitric acid and boil for about half an hour. Or, dissolve naphthalene in common nitric acid and let it stand 5–6 days (*Ann.*, 169, 82).

$\alpha$ -Nitro-naphthalene crystallizes from alcohol in yellow prisms, melts at  $61^\circ$ , and boils at  $304^\circ$ . Potassium permanganate oxidizes it to nitrophthalic acid (melting at  $210^\circ$ ).

Two **Dinitro-naphthalenes**,  $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ , are produced when nitronaphthalene is boiled with nitric acid. The so-called  $\alpha$ -compound (1, 5) consists of

colorless prisms, melting at  $217^{\circ}$ ; the  $\beta$ -body crystallizes in rhombic plates, and melts at  $170^{\circ}$ . A third dinitronaphthalene, from dinitronaphthylamine, melts at  $144^{\circ}$ . On boiling the dinitro-naphthalenes with fuming nitric acid, three trinitro- and two tetra-nitronaphthalenes result.

*Amido-naphthalenes*,  $C_{10}H_7.NH_2$ .

$\alpha$ -**Amido-naphthalene**,—naphthylamine, results from the reduction of  $\alpha$ -nitronaphthalene, and is obtained on heating  $\alpha$ -naphthol with  $CaCl_2$ -ammonia (p. 651). It consists of colorless needles or prisms, readily soluble in alcohol, melting at  $50^{\circ}$ , and boiling at  $300^{\circ}$ . It acquires a red color on exposure to the air, sublimes readily and possesses a pungent odor. It affords crystalline salts with acids. Oxidizing agents (chromic acid, ferric chloride, silver nitrate) produce a blue precipitate in the solutions of the salts: in a short time this changes into a red powder—oxynaphthamine,  $C_{10}H_9NO$ . When boiled with chromic acid, naphthylamine yields  $\alpha$ -naphthoquinone.

The nitration of the acet-compound (melting at  $159^{\circ}$ ), produces two **Nitronaphthylamines**,  $C_{10}H_6(NO_2).NH_2$ , of which the one melting at  $191^{\circ}$  (1, 4), affords  $\alpha$ -naphthoquinone upon oxidation; the elimination of its amido-group affords ordinary  $\alpha$ -nitronaphthalene ( $\alpha = 4$ ). When boiled with potassium hydroxide nitronaphthylamine yields  $\alpha$ -nitronaphthol—similar to the production of (1, 4)-nitrophenol from (1, 4)-nitraniline (p. 479). The second nitronaphthylamine melts at  $158^{\circ}$ , and when boiled with  $KOH$ , passes into  $\beta$ -nitronaphthol. Both no longer unite with acids.

The salts of **Diazo-naphthalene**,  $C_{10}H_7.N_2X$ , and of **Diazo-naphthalene-sulphonic acid**,  $C_{10}H_6\begin{smallmatrix} N_2 \\ \diagup \quad \diagdown \\ SO_3 \end{smallmatrix}$ , are perfectly analogous to the diazobenzenes and with anilines and phenols afford azo-coloring substances (p. 464).

Nitrous acid acting upon the cold alcoholic solution of  $\alpha$ -naphthylamine produces **Diazo-amido-naphthalene**,  $C_{10}H_7.N_2.NH$ .  $C_{10}H_7$ , crystallizing in brown leaflets, which, upon warming with acids decompose into  $\alpha$ -naphthol and  $\alpha$ -naphthylamine. If, however, nitrous acid acts upon alcoholic naphthylamine at ordinary temperatures, a molecular re-arrangement ensues (p. 463), and we obtain **Amido-azo-naphthalene**,  $C_{10}H_7.N_2.C_{10}H_6.NH_2$ .

In the preparation of the latter, the dilute aqueous solution of  $KOH$  (1 molecule), and  $KNO_2$  (1 molecule) is added to the cold saturated solution of naphthylamine hydrochloride (comp. p. 456). A brown precipitate separates, and is purified by crystallization from alcohol (*Ber.*, 7, 1290).

Amido-azo-naphthalene crystallizes in brown-red needles with a green metallic lustre, melts at  $174^{\circ}$ , and is readily soluble in alcohol; it dissolves with a dark blue color in concentrated sulphuric acid. It combines with one equivalent of acid to yellow and violet



colored salts, which are colored dark blue by concentrated acids (in the presence of alcohol). When heated together with naphthylamine-hydrochloride, it yields a base,  $C_{30}H_{21}.N_3$ :—



which corresponds perfectly to azodiphenyl-blue and belongs to the class of indulin colors (p. 470).

*Naphthalene red* (Magdala red) is the hydrochloric acid salt of this base,  $C_{30}H_{21}.N_3.HCl + H_2O$ , and appears in commerce as a dark brown powder, which is applied as a beautiful bright-red dye. It crystallizes in green metallic needles, and dissolves in alcohol with a red color. Its dilute solutions show a magnificent fluorescence. The alkyl iodides convert the salts into various other dyes. The alcoholic solution is decolorized on boiling with zinc dust, but is again colored red by exposure to the air.

**Azonaphthalene**,  $C_{10}H_7.N_2.C_{10}H_7$ , cannot be prepared from nitronaphthalene by reduction with alcoholic potash (p. 462). It does appear in small quantity when nitronaphthalene is heated with lime or zinc dust; it melts at  $280^\circ$ .

**$\beta$ -Naphthylamine**,  $C_{10}H_7.NH_2$ , was first obtained from nitro- $\alpha$ -brom-naphthalene when reduced with tin and hydrochloric acid, and is readily prepared with a little dinaphthylamine by heating  $\beta$ -naphthol to  $210^\circ$  with ammonia-zinc chloride (p. 432). It is further obtained by leading  $NH_3$  into heated  $\beta$ -naphthol. Phenyl-naphthylamine,  $C_{10}H_7.NH.C_6H_5$ , is similarly produced when  $\beta$ -naphthol is heated with aniline hydrochloride.  $\beta$ -Amido-naphthalene crystallizes from hot water in pearly leaflets, melting at  $112^\circ$ . It is odorless, and is not colored by oxidizing agents.

The **nitro- $\beta$ -amido-naphthalene**,  $C_{10}H_6 \begin{smallmatrix} \diagup NO_2 (1) \\ \diagdown NH_2 (2) \end{smallmatrix}$ , melts at  $123.5^\circ$ , and yields nitro- $\beta$ -naphthol when boiled with  $NaOH$ .

**Diamidonaphthalenes**,  $C_{10}H_6(NH_2)_2$ , have been obtained by the reduction of the dinitro- and nitro-amido-naphthalenes, and by the decomposition of amido-azo-naphthalenes (p. 465). The (1, 4)-compound, from (1, 4)-nitro-naphthalene, is readily oxidized to naphthoquinone.

On digesting four parts of naphthalene with three parts sulphuric acid at  $80^\circ$  we have formed  $\alpha$ - and  $\beta$ -**Naphthalene-sulphonic Acids**,  $C_{10}H_7.SO_3H$ , which may be separated by means of the barium or lead salts (*Ber.*, 3, 166); the salts of the  $\alpha$ -acid are much more readily soluble in water than those of the  $\beta$ -acid. The free acids are crystalline and deliquesce readily. When heated with sulphuric acid the  $\alpha$ -acid passes into the  $\beta$ -variety (similar to the orthophenol-sulphonic acid); therefore, the latter acid is exclusively produced at higher temperatures ( $160^\circ$ ). The  $\alpha$ -acid decomposes, upon heating with dilute hydrochloric acid to  $200^\circ$ , into naphthalene and sulphuric acid, whereas the  $\beta$ -acid

remains unaltered. The chloride of the  $\alpha$ -acid,  $C_{10}H_7SO_2Cl$ , is more readily soluble in ether, and melts at  $66^\circ$ , the chloride of the  $\beta$ -acid at  $76^\circ$ ; both yield crystalline leaflets. Zinc and sulphuric acid convert them into mercaptans,  $C_{10}H_7SH$ .

Protracted heating of naphthalene with sulphuric acid produces two **Naphthalene-disulphonic Acids**,  $C_{10}H_6(SO_3H)_2$ , from which two dicyanides,  $C_{10}H_6(CN)_2$ , are obtained on distillation with potassium cyanide.

#### *Phenol Derivatives.*

In the phenols of naphthalene the hydroxyls are far more reactive than in the benzene phenols. They readily yield amido-naphthalenes with  $NH_3$  (p. 462); and upon heating with alcohols and hydrochloric acid naphthol ethers result (*Ber.*, 15, 1427).

**$\alpha$ -Naphthol**,  $C_{10}H_7OH$ , results from  $\alpha$ -naphthylamine by means of the diazo-compound, and upon fusing  $\alpha$ -naphthalene-sulphonic acid with alkalis. Its formation from phenyl-isocrotonic acid (p. 646) is very noteworthy. It is soluble with difficulty in hot water, readily in alcohol and ether, crystallizes in shining needles, and has the odor of phenol. It melts at  $95^\circ$ , boils at  $278-280^\circ$ , and is readily volatilized. Ferric chloride precipitates violet flakes of dinaphthol,  $C_{20}H_{12}(OH)_2$ , from its aqueous solution. The acetate,  $C_{10}H_7O.C_2H_3O$ , melts at  $46^\circ$ ; the ethyl ether,  $C_{10}H_7O.C_2H_5$ , boils at  $270^\circ$ .

When the so-called nitroso- $\alpha$ -naphthols (p. 653) are oxidized with potassium ferricyanide two **Nitro- $\alpha$ -naphthols**,  $C_{10}H_6(NO_2).OH$ ,  $\alpha$  and  $\beta$ , result; these are also obtained when the two nitro- $\alpha$ -naphthylamines are boiled with caustic potash (p. 479). The  $\alpha$ -nitro-body (1, 4) melts at  $164^\circ$ ; its sodium salt was applied as *Campo Belio Yellow*. Its reduction affords **Amido- $\alpha$ -naphthol**,  $C_{10}H_6(NH_2).OH$  (1, 4), which is oxidized to  $\alpha$ -naphthoquinone by ferric chloride.

**$\beta$ -Nitro- $\alpha$ -naphthol** (1, 2) is very volatile with steam, and melts at  $128^\circ$  (*Ber.*, 15, 1815).

**Dinitro  $\alpha$ -naphthol**,  $C_{10}H_5(NO_2)_2.OH$ , is produced by the action of nitric acid upon  $\alpha$ -naphthol,  $\alpha$ -naphthol sulphonic acid, upon both nitro- $\alpha$ -naphthols, and upon  $\alpha$ -naphthylamine. It is obtained from the  $\alpha$ -naphthol-sulphonic acid by digestion with common nitric acid. It is almost insoluble in water, difficultly soluble in alcohol and in ether, crystallizes in fine, yellow needles, and melts at  $138^\circ$ . It decomposes alkaline carbonates, and affords yellow salts with one equivalent of base. The salts dye silk a beautiful golden-yellow. The sodium salt,  $C_{10}H_5(NO_2)_2.ONa + H_2O$ , finds use in dyeing, under the name of *naphthalene yellow* (Martius yellow). The potassium salt of dinitronaphthol-sulphonic acid,  $C_{10}H_4(NO_2)_2 \left\{ \begin{smallmatrix} SO_3K \\ OK \end{smallmatrix} \right.$ , obtained by the nitration of naphthol-trisulphonic acid, is the technically important *naphthol yellow*.

Further nitration of dinitronaphthol with nitric-sulphuric acid produces **Tri-nitronaphthol**,  $C_{10}H_4(NO_2)_3.OH$ , which crystallizes from glacial acetic acid in yellow needles or leaflets, melting at  $177^\circ$ . Its salts afford the same color as naphthalene yellow.

**$\beta$ -Naphthol**,  $C_{10}H_7.OH$ , from  $\beta$ -naphthalene-sulphonic acid and  $\beta$ -naphthylamine, is readily soluble in hot water, crystallizes in leaflets, melting at  $122^\circ$ , and boiling at  $286^\circ$ , and is very volatile. Ferric chloride imparts a greenish color to the solution and separates dinaphthol,  $C_{20}H_{12}(OH)_2$ , melting at  $216^\circ$ . The acetate melts at  $61^\circ$ .

By the oxidation of so-called nitroso- $\beta$ -naphthol (p. 653), we obtain  **$\alpha$ -Nitro- $\beta$ -naphthol**,  $C_{10}H_6(NO_2).OH$ , which is also formed from nitro- $\beta$ -naphthylamine, when it is boiled with sodium hydroxide. It consists of brown leaflets, melting at  $103^\circ$ . **Dinitro- $\beta$ -naphthol**,  $C_{10}H_5(NO_2)_2.OH$ , is obtained by the nitration of  $\beta$ -naphthol in alcoholic solution, and also from  $\beta$ -naphthylamine (*Ber.*, 17, 1171). It melts at  $195^\circ$ .

**Amido- $\beta$ -naphthol**,  $C_{10}H_6(NH_2).OH$  (1, 2), is obtained in the reduction of nitro- $\beta$ -naphthol (1, 2) with tin and hydrochloric acid; also from  $\beta$ -naphthol orange (see below) or from benzene azo- $\beta$ -naphthol by decomposition with tin and hydrochloric acid (*Ber.*, 16, 2861). It consists of white, shining, crystalline leaves, dissolves in ether with a beautiful violet fluorescence, and in ammonia with a yellow color, which, upon exposure, becomes dark-brown. Chromic acid oxidizes it to  $\beta$ -naphthoquinone.

On the addition of alcoholic  $\beta$ -naphthol to the solution of diazobenzene-sulphonic acid we get  **$\beta$ -Naphthol-azo-benzene-sulphonic Acid**,  $C_{10}H_6(OH).N_2.C_6H_4.SO_3H$ , whose sodium salt is the  *$\beta$ -Naphthol-orange—Tropæolin* (OOO) of commerce. The diazo-group occupies the ortho-place referred to hydroxyl (p. 465); tin and hydrochloric acid decompose the azosulphonic acid into amido- $\beta$ -naphthol (1, 2) and sulphanilic acid. By the conjugation of diazo-naphthalene sulphonic acid (p. 649), and  $\beta$ -naphthol (above), arises  **$\beta$ -Naphthol-azo-naphthalene-sulphonic Acid**,  $C_{10}H_6(OH).N_2.C_{10}H_6.SO_3H$ , whose sodium salt, the so-called *Pure red* or *Rocellin*, is used as a substitute for archil and cochineal. When mixed with  *$\beta$ -Naphthol-orange* (see above) it constitutes the so-called *rouge français*. By the conjugation of  $\beta$ -naphthol with azobenzene-disulphonic acids we get the *Bieberich scarlets* (p. 469).

The solution of  $\beta$ -naphthol in sulphuric acid produces a  **$\beta$ -Naphthol-sulphonic Acid**,  $C_{10}H_6(OH).SO_3H$ , whose sodium salt is *Croceïn yellow*. The conjugation of this with azobenzene-disulphonic acid (see above) affords *Croceïn scarlet* (*Ber.*, 15, 1352).

Dioxynaphthalenes,  $C_{10}H_6(OH)_2$ . Six of the ten possible isomerides are known; of these we mention those corresponding to the two naphthoquinones.

**$\alpha$ -Hydonaphthoquinone** (1, 4) is obtained from  $\alpha$ -naphthoquinone on boiling with hydriodic acid and phosphorus. It crystallizes from hot water in long needles, and melts at  $173^\circ$ . Chromic acid readily oxidizes it to  $\alpha$ -naphthoquinone.

**$\beta$ -Hydonaphthoquinone** (1, 2) separates in silvery leaflets, melting at  $60^\circ$ , when a solution of  $\beta$ -naphthoquinone in aqueous sulphurous acid stands for some time. It dissolves in the alkalis with a yellow color which becomes an intense green upon exposure.

**$\alpha$ -Naphthoquinone**,  $C_{10}H_6O_2$ , corresponding in every respect to benzoquinone (p. 503), is formed in the oxidation of  $\alpha$ -naphthylamine, nitro- $\alpha$ -naphthol, diamidonaphthalene (1, 4), and amido- $\alpha$ -naphthol (1, 4) with chromic acid (*Ber.*, 14, 1795); further, on heating naphthalene in glacial acetic acid with  $CrO_3$ . It crystallizes from hot alcohol in yellow rhombic plates, melting at  $125^\circ$ . It is perfectly similar to ordinary quinone, possesses the usual quinone odor, is very volatile, and distils over in a current of steam. Nitric acid oxidizes it to phthalic acid.

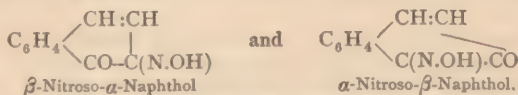
**$\alpha$ -Naphthoquinone Chlorimide**,  $C_{10}H_6$   $\begin{array}{c} O \\ \diagup \quad \diagdown \\ | \\ NCl \end{array}$ , obtained from amido- $\alpha$ -naphthol hydrochloride with a solution of bleaching lime (p. 505), consists of brown needles, melting at  $85^\circ$ . It yields  *$\alpha$ -Naphthol-blue* (p. 506), with dimethyl aniline.

So-called  **$\beta$ -Naphthoquinone**,  $C_{10}H_6O_2$ , is produced on oxidizing amido- $\beta$ -naphthol,  $C_{10}H_6(NH_2).OH$  (1, 2), with chromic acid (*Ann.*, 211, 49). It crystallizes from ether or benzene in orange-colored leaflets, and decomposes at  $115-120^\circ$ . It is distinguished from the real quinones (p. 503), by being odorless and non-volatile. It closely resembles anthraquinone, and even more phenanthraquinone (p. 656), like which it must be considered an ortho-diketone:—



In accordance with this it combines with one and two molecules of  $H_2N.OH$ , yielding the so-called nitroso-naphthols (see below). It dissolves with a yellow color in dilute alkalies and the solution becomes darker when shaken with air. Sulphurous acid reduces it at ordinary temperatures to  $\beta$ -naphtho-hydroquinone. Potassium permanganate oxidizes it to phthalic acid.

The so-called nitroso-naphthols, resulting from the action of nitrous acid upon the two naphthols (p. 485), represent *isonitroso-compounds* or *acetoxims* of diketones:—



$\alpha$ -Naphthol affords two isomeric nitroso-bodies,  $\alpha$ - and  $\beta$ -nitroso- $\beta$ -naphthol, the former melting, with decomposition, about  $165^\circ$ , the latter about  $145^\circ$ .  $\alpha$ -Nitroso- $\beta$ -naphthol is also obtained from  $\beta$ -naphthoquinone with hydroxylamine, and melts at  $109^\circ$ . The latter on heating yields, as does  $\beta$ -nitroso- $\alpha$ -naphthol, one and the same product,  $C_{10}H_6N_2O$ , which is to be considered as the anhydride of the di-isonitroso-compound (*Ber.*, 17, 803).

**Dioxynaphthoquinone**,  $C_{10}H_4(O_2)(OH)_2$ , **Naphthalizarin**, corresponding to anthracene-alizarin, is produced when  $\alpha$ -dinitro-naphthalene is heated with



concentrated sulphuric acid and zinc. It sublimes in red needles with green metallic reflex, dissolving in alcohol with a red, in ammonia with a bright blue color, and yields, like alizarin, violet blue precipitates with baryta and lime water.

We obtain the corresponding cyanides or nitriles by the distillation of the alkali salts of the naphthalene-disulphonic acids, or the phosphoric esters of the naphthols with potassium cyanide (p. 525).

**$\alpha$ -Cyan-naphthalene**,  $C_{10}H_7.CN$ , has also been prepared from naphthyl formamide,  $C_{10}H_7.NH.CO.H$  (from naphthylamine oxalate) (comp. p. 441). It dissolves readily in alcohol, and forms flat needles, melting at  $37.5^\circ$ , and distilling at  $298^\circ$ .  **$\beta$ -Cyan-naphthalene**, from  $\beta$ -naphthalene sulphonic acid, crystallizes in yellow prisms, melts at  $61^\circ$ , and distils at  $304^\circ$ .

Similarly, two **naphthalene-dicyanides**,  $C_{10}H_6(CN)_2$ , are produced from the two naphthalene disulphonic acids. Both sublime in shining needles; the  $\alpha$ -compound melts at  $268^\circ$  and is almost insoluble in the ordinary solvents; the  $\beta$ -dicyanide dissolves in hot alcohol, and melts at  $297^\circ$ .

Naphthalene carboxylic acids are produced on saponifying the cyan-naphthalenes with alcoholic potassium hydroxide.

**$\alpha$ -Naphthoic Acid**,  $C_{10}H_7.CO_2H$ , from  $\alpha$ -cyan-naphthalene, is also prepared by fusing potassium  $\alpha$ -naphthalene sulphonate with sodium formate, and by the action of sodium amalgam on a mixture of brom-naphthalene and chlor-carbonic ester. It consists of fine needles, melting at  $160^\circ$ , and dissolving in hot water with difficulty, but readily in hot alcohol. Distilled with baryta it breaks up into naphthalene and  $CO_2$ .

Its *ethyl ester* is a liquid boiling at  $309^\circ$ . The *chloride*,  $C_{10}H_7.CO.Cl$ , boils at  $297^\circ$ .

**$\beta$ - or Iso-naphthoic Acid**,  $C_{10}H_7.CO_2H$ , from  $\beta$ -cyan-naphthalene, crystallizes from hot water in long, silky needles, and melts at  $182^\circ$ .

A **dihydronaphthoic acid**,  $C_{10}H_7(H_2).CO_2H$ , has been synthetically prepared from benzyl aceto-acetic ester (p. 645); it yields phthalic acid when oxidized.

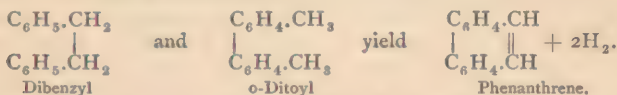
**$\alpha$  Naphthoyl formic Acid**,  $C_{10}H_7.CO.CO_2H$ , obtained from  $\alpha$ -naphthoyl chloride by means of the cyanide (p. 546), melts at  $113^\circ$ , and affords  **$\alpha$ -naphthyl acetic acid**,  $C_{10}H_7.CH_2.CO_2H$ , when reduced, which melts at  $131^\circ$ , and by the splitting off of  $CO_2$  passes into  $\beta$ -methyl-naphthalene.

**Hydroxynaphthoic Acids**,  $C_{10}H_6(OH)CO_2H$ , naphthol carboxylic acids, arise from the two naphthols when they are treated with  $CO_2$  and sodium; also from sulphonaphthoic acids by fusion with alkalis. In this way six isomerides have been obtained.

**Naphthalene-Dicarboxylic Acids**,  $C_{10}H_6(CO_2H)_2$ . Six of the ten possible isomerides are known. When acenaphthene and ace naphthylene are oxidized with chromic acid we get **Naphthalic Acid**, which (like phthalic acid) decomposes at  $140$ – $150^\circ$  without melting into water, and its anhydride,  $C_{10}H_6(CO)_2O$ , crystallizing from alcohol in needles, and melting at  $266^\circ$ . Ignited with lime, the acid decomposes into  $CO_2$  and naphthalene.

Phenanthrene,  $C_{14}H_{10}$ .

Phenanthrene (p. 645), occurs in coal-tar and in the so-called "stubb," a mass of substance obtained (together with fluoranthene) in the distillation of mercury ores in Idria. It is prepared synthetically (with diphenyl, anthracene and other hydrocarbons) from various benzene compounds, by conducting their vapors through a red-hot tube, *e. g.*, from toluene, stilbene, diphenyl and ethylene, from dibenzyl and ortho-ditolyl:—

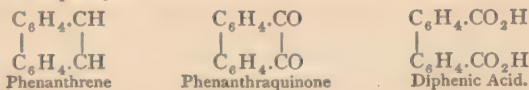


Sodium acting on ortho-brombenzyl bromide,  $C_6H_4Br \cdot CH_2 \cdot Br$ , also produces it (together with anthracene, p. 635).

Phenanthrene is obtained from crude anthracene by taking that fraction boiling at  $320-350^\circ$ , concentrating it by further distillation, and crystallizing from alcohol, when anthracene will separate first. The phenanthrene is obtained from its picric acid compound, or by oxidation with chromic acid, when the anthracene will be first attacked (*Ann.*, 196, 34).

Phenanthrene crystallizes in colorless, shining leaflets or plates, melting at  $99^\circ$ , boiling at  $340^\circ$ , and subliming readily. It dissolves in 50 parts alcohol at  $14^\circ$ , in 10 parts (95 per cent.) on boiling, and readily in ether and benzene. The solutions exhibit a blue fluorescence. The picric acid compound,  $C_{14}H_{10} \cdot C_6H_2(NO_2)_3 \cdot OH$ , separates in yellow needles on mixing the alcoholic solutions, and melts at  $144^\circ$ . Phenanthrene is oxidized by boiling with chromic acid to phenanthraquinone, then to diphenic acid.

Phenanthrene must, from its formation from dibenzyl and ortho-brombenzyl bromide, be considered a diphenyl derivative, in which two ortho-places of the two benzene nuclei are united by the group  $C_2H_2$ ; the latter, therefore, forms, with the four carbon atoms of the two benzene rings, a third normal benzene ring. So-called phenanthraquinone, the oxidation product of phenanthrene, must be regarded as an ortho-diketone (p. 503), because further oxidation converts it into diphenic acid (p. 604), in which the two carboxyl groups are inserted in two ortho-places of diphenyl:—



Hydrogen addition products result from heating phenanthrene with hydriodic acid and phosphorus. The tetra-hydride,  $C_{14}H_{14}$ , boils at  $310^\circ$ , and solidifies on cooling. Chlorine produces substitution products, of which the *octo chloride* melts at  $270-280^\circ$ , and by further chlorination (comp. p. 421) is split into hexachlorbenzene,  $C_6Cl_6$ , and  $CCl_4$ . Bromine combines with phenanthrene in  $CS_2$  solution, yielding the *dibromide*,  $C_{14}H_{10} \cdot Br_2$ , which melts at  $98^\circ$ , with decom-

position, and readily breaks up into HBr and *bromphenanthrene*,  $C_{14}H_9Br$ . This melts at  $63^\circ$ , and is oxidized to phenanthraquinone by chromic acid.

Ordinary nitric acid converts phenanthrene into three *nitrophenanthrenes*,  $C_{14}H_9(NO_2)$ , which afford three *amido-phenanthrenes*,  $C_{14}H_9(NH_2)$ , by reduction.

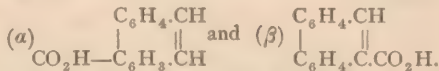
Two *phenanthrene-sulphonic acids*,  $C_{14}H_9.SO_3H$ , are reduced on digesting phenanthrene with sulphuric acid. If these be distilled with yellow prussiate of potash we obtain two *cyanides*,  $C_{14}H_9.CN$ , yielding the corresponding carboxylic acids.

**Phenanthraquinone**,  $C_{14}H_8O_2$ , an ortho-diketone (see above), is formed in the action of  $CrO_3$  upon phenanthrene in glacial acetic acid solution; more readily by heating it with a chromic acid mixture (*Ann.*, 196, 38). It crystallizes from alcohol in long, orange-yellow needles, melts at  $198^\circ$ , and distils without decomposition. It is not very soluble in hot water or cold alcohol, but readily in hot alcohol, ether and benzene. It dissolves in concentrated sulphuric acid with a dark green color, and is reprecipitated by water. By adding toluene containing thiotolene and sulphuric acid to the acetic acid solution of phenanthraquinone a bluish-green coloration is produced (p. 399).

Like  $\beta$ -naphthaquinone phenanthraquinone is odorless, not volatile in steam, and is readily reduced by sulphurous acid. Like the latter, too, it unites with one and two molecules of  $H_2N.OH$  to perfectly corresponding isonitroso-compounds (p. 653). Being a ketone it also combines with primary sodium sulphite to the crystalline derivative,  $C_{14}H_8O_2.SO_3HNa + 2H_2O$ , from which it is again separated by alkalis or acids. By oxidation with chromic acid, or by boiling with alcoholic potash, phenanthraquinone is oxidized to diphenic acid; ignition with soda-lime produces diphenylene ketone (p. 604), fluorene and diphenyl. Diphenylene glycollic acid (p. 605), fluorene alcohol and diphenylene ketone are obtained on boiling with aqueous soda-lye. Ignited with zinc dust we obtain phenanthrene.

On digesting phenanthraquinone with concentrated sulphurous acid it changes to **Dioxypheanthrene**,  $C_{14}H_8(OH)_2$  (Phenanthrene-hydroquinone), which crystallizes from hot water in colorless needles that turn brown on exposure, and reoxidize to phenanthraquinone. The diacetate crystallizes from benzene in plates, melting at  $202^\circ$ .

By saponifying the two phenanthrene cyanides we obtain two **Phenanthrene-carboxylic Acids**,  $C_{15}H_{20}O_2$  :—



The  $\alpha$ -acid melts at  $266^\circ$ , and is oxidized to phenanthraquinone carboxylic acid,  $C_{14}H_7(O_2).CO_2H$ , by chromic acid; the  $\beta$ -acid melts at  $251^\circ$ , and yields phenanthraquinone.

Besides the hydrocarbons with high boiling points which have been derived from coal-tar and already described: naphthalene,  $C_{10}H_8$  ( $218^\circ$ ); methyl-naphthalene,  $C_{11}H_{10}$  ( $218^\circ$ ); acenaphthene,  $C_{12}H_{10}$  ( $278^\circ$ ); fluorene,  $C_{13}H_{20}$  ( $305^\circ$ ); phenanthrene,  $C_{14}H_{10}$

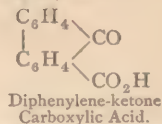
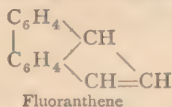
(340°), and anthracene,  $C_{14}H_{10}$  (360°), we have the following: fluoranthene,  $C_{15}H_{10}$ ; pyrene,  $C_{16}H_{10}$ , and chrysene,  $C_{18}H_{12}$ . These have been isolated from the so-called crude phenanthrene, the fraction boiling above 360°.

Fluoranthene and pyrene occur chiefly in the first fractions. They are separated by fractional distillation under diminished pressure; fluoranthene boiling at 250° under 60 mm. pressure; pyrene at 260°. Their perfect separation is then effected by the fractional crystallization of their picric acid derivatives (*Ann.*, 200, 1). The portions boiling at the most elevated temperatures consist mainly of pyrene and chrysene, which are separated by means of carbon disulphide (which dissolves pyrene) and by the crystallization of their picric acid combinations (*Ann.*, 158, 285 and 299).

Pyrene and fluoranthene (idryl) also occur in the "stubb-fat" obtained from the distillation of the "stubb" (p. 655).

**Fluoranthene**,  $C_{15}H_{10}$ , **Idryl**, crystallizes from alcohol in needles or plates, melting at 109–110°, and dissolves readily in hot alcohol, ether and  $CS_2$ . It dissolves with a blue color in warm sulphuric acid. Its picric acid compound,  $C_{15}H_{10} \cdot C_6H_3(NO_2)_3OH$ , consists of reddish-yellow needles, is difficultly soluble in ether, and melts at 182°. Fuming nitric acid converts idryl into the trinitro-compound,  $C_{15}H_7(NO_2)_3$ , melting above 300°. **Fluoranthraquinone**,  $C_{15}H_8O_2$ , is obtained by oxidizing idryl with chromic acid. It crystallizes from alcohol in small, red needles, melting at 188°, and dissolves, like phenanthrene, in alkaline bisulphites. If the quinone be further oxidized (with elimination of  $CO_2$ ) we obtain diphenylene-ketone carboxylic acid,  $C_{14}H_6O_2$ , crystallizing in orange-red needles, and melting at 191°. When fused with KOH it yields iso-diphenic acid (p. 604), and when heated with lime it decomposes into  $CO_2$  and diphenylene ketone.

The constitution of fluoranthene and of diphenylene ketone-carboxylic acid probably corresponds to the formulas (*Ann.*, 200, 20):—



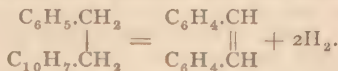
**Pyrene**,  $C_{16}H_{10}$ , is difficultly soluble in hot alcohol (33 parts), readily in ether, benzene and  $CS_2$ , crystallizes in colorless leaflets or plates, and melts at 148°. The picric acid compound crystallizes from alcohol in long needles, and melts at 222°. Chromic acid oxidizes it to **Pyrenquinone**,  $C_{16}H_8O_2$ , a brick-red powder, which sublimates in red needles. It dissolves with a brown color in sulphuric acid.

**Chrysene**,  $C_{18}H_{12}$ , is generally colored yellow (hence the name), but can be rendered perfectly colorless by the action of different reagents. It is very difficultly soluble in alcohol, ether and  $CS_2$ , and rather readily soluble in hot benzene and glacial acetic acid; it melts at 250°, and boils at 436°. It crystallizes and sublimates in silvery leaflets, which exhibit an intense violet fluorescence. The picric acid compound crystallizes from hot benzene in red needles, and is decomposed by alcohol. When digested with chromic acid and glacial acetic acid it



oxidizes to so-called **Chrysoquinone**,  $C_{18}H_{10}O_2$  (a diketone), which crystallizes in red needles, melting at  $235^\circ$ , and dissolving in sulphuric acid with a blue color; water reprecipitates chrysoquinone. It unites as a ketone with primary sodium sulphite. Sulphurous acid reduces it to hydroquinone,  $C_{18}H_{10}(OH)_2$ . The distillation of chrysoquinone with soda-lime affords the hydrocarbon,  $C_{18}H_{12}$  (Phenylnaphthalene,  $C_{10}H_7 \cdot C_6H_5$ ). This is similar to the production of diphenyl from phenanthraquinone (p. 655).

Chrysene is prepared synthetically from benzyl-naphthyl-ketone,  $C_6H_5 \cdot CH_2 \cdot CO \cdot C_{10}H_7$  (from phenyl acetic chloride,  $C_6H_5 \cdot CH_2 \cdot COCl$ , and naphthalene with  $AlCl_3$ ), if the latter be converted by heating with hydriodic acid and phosphorus into the hydrocarbon,  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_{10}H_7$ , and then distilling this through a red-hot tube—just as phenanthrene is produced from dibenzyl:—



Therefore, chrysene consists, in all probability, of four unsymmetrical, condensed benzene nuclei.

A hydrocarbon termed **Retene**,  $C_{18}H_{16}$ , occurs in the tar of pines, rich in resin and in some varieties of mineral tar. It is very soluble in alcohol and benzenes, crystallizes in pearly leaflets, melts at  $98^\circ$ , boils at about  $390^\circ$ , and volatilizes readily with steam. Its picric acid compound crystallizes in orange-yellow needles, and melts at  $123^\circ$ . Chromic acid oxidizes *retene* to phthalic acid, acetic acid, and so-called *dioxyretistene*,  $C_{16}H_{14}O_2$ , a red powder, which crystallizes in orange-yellow needles, melts at  $194^\circ$ , and sublimes readily. It dissolves in sulphuric acid with a dark green color. If dioxyretistene be distilled with zinc dust, it affords the hydrocarbon *retistene*,  $C_{16}H_{14}$ , which melts at  $57^\circ$  (*Ber.*, 17, 455 and 696).

**Schererite** and **fichtelite** are similar hydrocarbons found in lignite and pine woods. The **Idrialin**, occurring in the mercury ores of Idria, possesses the formula,  $C_{40}H_{28}O$ .

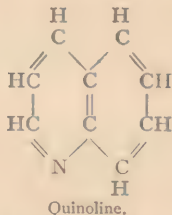
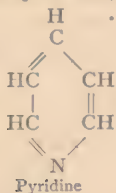
**Picene**,  $C_{22}H_{14}$ , is a hydrocarbon formed by the distillation of lignite, coal-tar and petroleum residues. It is very difficultly soluble in most of the solvents, but most readily in cumene, crystallizes in blue fluorescing leaflets, melting at  $338^\circ$ , and boils at  $519^\circ$ . It dissolves with a green color in sulphuric acid and is oxidized by chromic acid to an orange-red quinone.

## PYRIDINE AND QUINOLINE GROUPS.

Pyridine,  $C_5H_5N$ , and Quinoline,  $C_9H_7N$ , are two basic bodies, which command particular interest, because they have been recognized as the parent substances of many alkaloids. In their entire deportment they closely resemble the benzene compounds. By replacing the hydrogen in them with alkyls (especially methyls) they yield a series of homologous compounds—the *Pyridine* and *Quinoline bases*, e. g.,  $C_5H_4(CH_3)N$ , and  $C_9H_6(CH_3)_2N$ , from which acids (mono- di- and tri-carboxylic acids) result on oxidizing the methyl groups. By elimination of the carboxyls from the acids, the stable parent nuclei, pyridine and quinoline, are regenerated. This deportment, characteristic of benzene compounds, is explained by the

constitution of pyridine and quinoline. Both contain a closed chain consisting of five carbon-atoms and one nitrogen-atom, which is characterized by especial stability,—similar to the pyrrol and indol bodies, which are constructed upon a group made up of four carbon-atoms and one nitrogen-atom (p. 399 and p. 589).

We can regard pyridine,  $C_5H_5N$ , as a benzene in which one CH-group is replaced by a nitrogen atom, whereas quinoline,  $C_9H_7N$ , is derived in a similar manner from naphthalene,  $C_{10}H_8$  :—



The constitution of quinoline has been positively established by numerous synthetic methods (p. 667); that of pyridine is determined from its formation from quinoline. By the oxidation of the latter, the benzene nucleus is destroyed (as with naphthalene, p. 647), the  $\alpha$ - $\beta$ -pyridine-dicarboxylic acid,  $C_5H_3N(CO_2H)_2$ , formed and when it splits off  $2CO_2$  pyridine is produced. The synthetic methods for preparing the pyridines (p. 660), at present known, do not distinctly indicate the constitution of the pyridine nucleus, but do, however, agree in all respects with the constitution deduced from quinoline.

As to the supposition, that the nitrogen-atom in both pyridine and in quinoline (with the same ring-linking) is connected with three carbon-atoms, see *Ber.*, **16**, 1974 and 2063, **17**, 1521.

Since the nitrogen-atom in the pyridine and quinoline bases is joined with three affinities to carbon, these compounds are tertiary amines, which combine with alkyl iodides, yielding ammonium iodides. Further, it follows, from the accepted structural formulas, that the pyridine and quinoline derivatives are capable, like benzene, of yielding hydrogen addition products; thus from pyridine, we obtain a hexa-hydrate,  $C_5H_5(H_6)N$ , identical with the alkaloid piperidine,  $C_5H_{11}N = C_5H_{10}:NH$ , and this is again converted by oxidation into pyridine. The possible isomeric derivatives are similarly deduced from the structural formulas and are fully verified by the facts already alluded to (p. 661).

## 1. PYRIDINE GROUP— $C_nH_{2n-5}N$ .

PYRIDINE,  $C_5H_5N$ .

Picoline— $C_6H_7N = C_5H_4(CH_3)N$ —Methyl pyridine.

Lutidine— $C_7H_9N = C_5H_3(CH_3)_2N$ —Dimethyl pyridine.

Collidine— $C_8H_{11}N = C_5H_2(CH_3)_3N$ —Trimethyl pyridine.

The following little investigated bases, isolated from coal-tar, are also included

here: *Parvoline*,  $C_9H_{13}N$  (B. P.,  $188^\circ$ ); *Corindine*,  $C_{10}H_{15}N$  (at  $211^\circ$ ), and *Rubidine*,  $C_{11}H_{17}N$  (at  $230^\circ$ ).

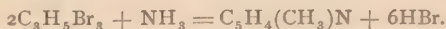
The pyridine bases arise in the dry distillation of nitrogenous carbon compounds and occur simultaneously with the quinoline bases in coal-tar (along with the isomeric anilines) and especially in bone-oil.

To obtain the pyridine bases from Dippel's oil (p. 401), concentrate the dilute sulphuric acid solution (when any pyrrol, which has dissolved, will be volatilized or resinified), separate the pyridine bases by means of concentrated sodium hydroxide, dehydrate them with caustic soda and subject the product to fractional distillation (*Ber.*, 12, 1989). Consult *Ber.*, 16, 2977, upon the pyridine bases of coal-tar.

Again, the pyridines, as well as quinoline bases are obtained by the distillation of the alkaloids (cinchonine) with caustic alkali, or by oxidizing the quinoline bases and alkaloids to pyridine carboxylic acids, *e. g.*,  $C_8H_8N(CO_2H)_2$ , which split off  $CO_2$  (see above) and yield pyridines.

#### Synthetic methods of forming the Pyridines :—

*a. Methyl pyridine*,  $C_5H_4(CH_3)N$ , is prepared from acrolein-ammonia,  $C_3H_5NO$ , by elimination of water (p. 159), or by heating tribrom-allyl with alcoholic- $NH_3$  to  $250^\circ$  :—

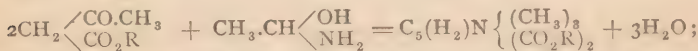


*Trimethyl-pyridine*,  $C_5H_2(CH_3)_3N$  (aldehydine, p. 663), is obtained from ethylene chloride or bromide with alcoholic ammonia, or from aldehyde by heating the oxytetraldine which first forms (p. 159).

*$\beta$ . Methyl pyridine*, is obtained from glycerol and acetamide (or other amides) by heating with  $P_2O_5$  (*Ber.*, 15, 528).

*Chlor- and Brom-pyridine*,  $C_5H_4BrN$ , result on heating pyrrol-potassium with  $CHCl_3$  and  $CHBr_3$  (p. 400). Pyridine,  $\gamma$ -oxypyridine,  $C_5H_4(OK)N$ , and methyl pyridine are also obtained from the ammonia compounds of chelidonic, meconic and comenic acids (p. 368).

The ready formation of trimethyl-dihydro-pyridine-dicarboxylic ester  $C_5H_2N(CH_3)_3(CO_2R)_2$ , on digesting aceto-acetic ester with aldehyde ammonia, is very interesting :—



here the nitrogen of the  $NH_2$ -group arranges itself in the para-place, referred to the entering aldehyde-radical (*Ber.*, 17, 1521). The oxidation of the dihydro-compound with nitrous acid affords the ester of normal **Trimethyl-pyridine-dicarboxylic Acid**,  $C_5N(CH_3)_3(CO_2H)_2$ , from which is obtained a series of pyridine carboxylic acids (p. 666), by the successive oxidation of the methyls and the elimination of  $CO_2$ . (*Ann.*, 215, 1, and *Ber.*, 16, 1946.)

The dimethyl-phenyl-dihydro-pyridine-dicarboxylic ester,  $C_5H_2N(CH_3)_2C_6H_5(CO_2R)_2$ , is produced in a similar manner from aceto-acetic ester (2 molecules) with benzaldehyde and alcoholic ammonia. The oxidation of the methyls and elimination of  $CO_2$  from this compound yield  $\gamma$  phenyl-pyridine,  $C_5H_4(C_6H_5)N$  (*Ber.*, 16, 1604 and 17, 1515).

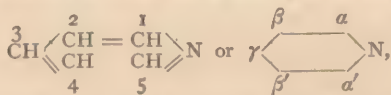
The pyridine bases are colorless liquids with a peculiar odor. Pyridine,  $C_5H_5N$ , is miscible with water. The solubility of the higher members grows rapidly less. They form crystalline salts with one equivalent of the acids. They are attacked with difficulty when boiled with nitric or chromic acid, and by this behavior are easily distinguished from the isomeric anilines. In the homologous pyridines, however, the alkyls are oxidized to carboxyls by a potassium permanganate solution.

The pyridines combine, as tertiary bases, with the alkyl iodides, yielding ammonium iodides. The ammonium hydroxides, obtained from the latter by means of silver oxide, sustain a complicated decomposition when exposed to heat (Consult *Ber.*, 17, 1027, upon the deportment of the ammonium hydroxides of the pyridine-carboxylic acids).

If the ammonium iodides be heated with NaOH, an extremely pungent odor is developed—*Reaction for the pyridine bases* (*Ber.*, 17, 827). Some of the pyridines yield hydrides with nascent hydrogen (p. 659); their ammonium hydroxides are decomposed by further reactions into trimethylamine and a hydrocarbon (see piperidine and conine).

Pyridine heated with hydriodic acid to  $300^\circ$ , yields normal pentane,  $C_5H_{12}$ , and collidine, under the same treatment, affords normal octane (*Ber.*, 16, 591). Metallic sodium causes the pyridines to undergo a peculiar polymerization, and they then yield *dipyridine bases*.

The derivatives produced by the replacement of the hydrogen atoms in pyridine can easily be deduced in their possible isomerisms from the given structural formulas (p. 659), and are perfectly analogous to the isomerisms of the benzene derivatives. Representing the five hydrogen atoms, or the affinities of the pyridine nucleus, with numbers or letters, corresponding to the diagram:—



then the positions, 1 and 5, also 2 and 4 (as in benzene), are similar (p. 406). The first may be designated the ortho-, the latter, the meta-positions—while the position 3, occurring only once, corresponds to the *para* of benzene. From this we conclude, that the mono-derivatives of pyridine,  $C_5H_4(X)N$ , can exist in three series, while six isomerides are possible with the di-derivatives  $C_5H_3(X_2)N$ . This is verified by the existence of three methyl-, three propyl- and phenyl-pyridines,  $C_5H_4(R)N$ , of three pyridine-mono-carboxylic acids,  $C_5H_4(CO_2H)N$ , of six dicarboxylic acids, etc. For practical reasons the isomerides are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -derivatives, corresponding with the second diagram. By the oxidation of the two phenyl-pyridines,  $C_5H_4(C_6H_5)N$ ,  $\alpha$ - and  $\beta$ -obtained from the two naphthoquinolines, and of the third  $\gamma$ -phenyl-pyridine, it is evident that the  $\alpha$ -place corresponds to the position 1 (= 5), the  $\beta$ - to the position 2 (= 4) and the  $\gamma$ - to the position 3 (*Monatshefte für Chemie*, IV, 437 and *Ber.*, 17, 1518).

The  $\gamma$ - or para-derivatives of pyridine are, like the para-benzene compounds, mostly more difficultly soluble and more difficultly fusible than the  $\alpha$ - or ortho-compounds.



**Pyridine**,  $C_5H_5N$ , can be prepared from bone-oil, and is obtained from all the pyridine-carboxylic acids on distillation with lime. It is a pungent-smelling liquid, miscible with water, of sp. gr. 0.986 at  $0^\circ$ , and boiling at  $116.7^\circ$ . Its hydrochloride,  $C_5H_5N.HCl$ , is deliquescent, and with platinum chloride affords a difficultly soluble double salt,  $(C_5H_5N.HCl)_2.PtCl_4$ . Sodium amalgam, or better, sodium and alcohol, convert it into the hexahydride—piperidine,  $C_5H_{11}N$  (p. 677), from which, vice versa, pyridine is obtained by oxidation.

Pyridine affords ammonium iodides with alkyl iodides (p. 661). It combines with chloracetic acid and yields **Pyridine-betaïne**,  $C_5H_5N \begin{smallmatrix} \text{CH}_2.CO \\ \diagup \quad \diagdown \\ O \end{smallmatrix}$ , corresponding fully to ordinary betaïne.

Sodium converts pyridine into polymeric **Dipyridine**,  $C_{10}H_{10}N_2$ , an oil boiling at  $286-290^\circ$ ;  $MnO_4K$  oxidizes it to isonicotinic acid. At the same time rather large quantities of **p-Dipyridyl**,  $C_{10}H_8N_2 = NC_5H_4.C_5H_4N$ , are produced; this distils at  $304^\circ$ , sublimes in long needles, and melts at  $114^\circ$ . It is a di-acidic base.  $MnO_4K$  oxidizes it to isonicotinic acid. **Isonicotine**,  $C_{10}H_{14}N_2$ , is obtained from it by reduction with tin and hydrochloric acid. It melts at  $78^\circ$  (*Ber.*, 16, 423). Isomeric **m-Dipyridyl**,  $C_{10}H_{12}N_2$ , results from meta-dipyridyl-dicarboxylic acid (from phenanthroline, p. 667), boils at  $293^\circ$ , and yields deliquescent needles.  $MnO_4K$  oxidizes it to nicotinic acid. Reduction with tin and hydrochloric acid affords nicotidine,  $C_{10}H_{14}N_2$ , isomeric with nicotine, and boiling at  $288^\circ$  (*Ber.*, 16, 2521).

**Chlor- and Brom-pyridine**,  $C_5H_4BrN$ , have been obtained from pyrrol (p. 660). **Brom-pyridine** and **Dibrom-pyridine**,  $C_5H_3Br_2N$ , are produced on brominating pyridine and aceto-piperidine (*Ber.*, 16, 587), and also pyridine-sulphonic acid.

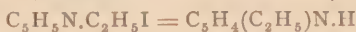
If pyridine be heated with concentrated sulphuric acid to  $330^\circ$ , or with fuming sulphuric acid (*Ber.*, 17, 763) we get  **$\beta$ -Pyridine sulphonic Acid**,  $C_5H_4N.SO_3H$ , whose barium salt,  $(C_5H_4N.SO_3)_2Ba + 4H_2O$ , crystallizes in silky needles;  **$\beta$ -Cyan pyridine**,  $C_5H_4N.CN$ , produced on distilling the sodium salt with potassium cyanide, crystallizes in white needles, melts at  $48-49^\circ$ , and by saponification yields nicotinic acid.

**Oxypyridines**,  $C_5H_4(OH)N$ .

**$\alpha$ -Oxypyridine** (1) is obtained from oxyquinolic acid (p. 665) on distilling its silver salt; it melts at  $107^\circ$ , and is colored red by ferric chloride (*Ber.*, 17, 592).  **$\beta$ -Oxypyridine** (2) results from the fusion of pyridine-sulphonic acid with  $KOH$ ; it melts at  $123^\circ$ , and is colored red by ferric chloride.  **$\gamma$ -Oxypyridine** (Pyridone) is obtained from oxypicolinic acid (from comenic acid) and from oxyquinolic acid by the elimination of  $CO_2$ . It melts at  $148^\circ$ , and ferric chloride imparts a yellowish color to it (*Ber.*, 17, Ref. 169).

A **dioxypyridine**,  $C_5H_3(OH)_2N$  (pyrocomenamic acid) results from dioxypicolinic acid (comenamic acid, p. 664) and crystallizes from water in thick needles (*Ber.*, 16, 1373).

The methylated pyridines occur in bone-oil. They are synthetically prepared by heating the pyridine-ammonium-iodides to  $300^\circ$  (*Ber.*, 16, 2059; 17, 772):—



This is analogous to the formation of the homologous anilines from the alkyl anilines (p. 433). They also result from the alkyl piperidines by the splitting-off of hydrogen (p. 677 and *Ber.*, 17, 825).

**Methyl Pyridines**,  $C_5H_4(CH_3)N$ , Picolines.

$\alpha$ - and  $\beta$ -Methyl Pyridine occur in bone oil, and may be separated by means of their  $PtCl_4$  salts. The  $\beta$ -body has been obtained from glycerol and acetamide (p. 660). The former boils at  $134^\circ$ , and is oxidized by  $MnO_4K$  to picolinic acid; the latter boils at  $140^\circ$ , and yields nicotinic acid.  $\gamma$ -Methyl Pyridine has been synthesized from acrolein-ammonia and from tribromallyl (p. 660); judging from its  $PtCl_4$  salt it differs from the  $\alpha$ - and  $\beta$ -varieties.

**Dimethylpyridines**,  $C_5H_3(CH_3)_2N$ , Lutidines.

Two dimethyl pyridines occur in the fraction of Dippel's oil, boiling at  $150$ – $170^\circ$ . When they are oxidized with  $MnO_4K$  they yield lutidinic acid and isocinchomeric acid,  $C_5H_3N(CO_2H)_2$  (*Ber.*, 13, 2422).

**Ethyl Pyridines**,  $C_5H_4(C_2H_5)N$ .

$\alpha$ -Ethyl pyridine is prepared, together with the  $\gamma$ -, on heating pyridine-ethyl iodide (see above). It boils at  $166^\circ$ , and yields picolinic acid when oxidized.  $\beta$ -Ethyl pyridine has been obtained from cinchonine and brucine on heating with  $KOH$ . It boils at  $165^\circ$ , and yields nicotinic acid.  $\gamma$ -Ethyl pyridine, produced together with the  $\alpha$ -, boils at  $152^\circ$ , and yields isonicotinic acid (*Ber.*, 17, 772).

**Trimethyl Pyridines**,  $C_5H_2(CH_3)_3N$ , Collidines.

Different collidines have been obtained from bone-oil, and by the distillation of cinchonine and other alkaloids with  $KOH$ . Aldehydine, derived from aldehyde-ammonia and ethylidene chloride (p. 660) boils at  $180$ – $182^\circ$ , and by partial oxidation with chromic acid forms picoline-dicarboxylic acid,  $C_5H_2(CH_3)N(CO_2H)_2$ . Collidine results from synthetic collidine-dicarboxylic acid,  $C_5(CH_3)_3N(CO_2H)_2$ , by distillation with lime. It boils at  $171$ – $172^\circ$ .

**Propyl Pyridines**,  $C_5H_4(C_3H_7)N = C_8H_{11}N$ .

$\alpha$ -Propyl Pyridine is obtained, together with the  $\gamma$ -, on heating pyridine-propyl iodide (see above), and boils at  $173$ – $175^\circ$ .  $\gamma$ -Propyl Iodide boils at  $160$ – $164^\circ$ , and yields isonicotinic acid. When sodium acts on the alcoholic solution both propyl pyridines yield corresponding Propyl-hexahydropyridines,  $C_8H_{17}N$ , Propyl-piperidines (p. 678), which are very similar to the isomeric conine (*Ber.*, 17, 762).

In a similar manner we get from pyridine-isopropyl iodide  $\alpha$ - and  $\gamma$ -Isopropylpyridine,  $C_5H_4(C_3H_7)N$ ; the  $\alpha$ - boils at  $166$ – $168^\circ$ , and by oxidation yields picolinic acid; the  $\gamma$ -body boils at  $158^\circ$ , and affords isonicotinic acid. The addition of  $6H$  to these converts them into the corresponding isopropyl-piperidines,  $C_8H_{17}N$  (see above), of which the  $\alpha$ -compound is distinguished from conine almost solely by its optical inactivity (*Ber.*, 17, 1676).

$\beta$ -Isopropyl pyridine appears to be a base, formed by distilling nicotine,  $C_{14}H_{19}N_2$ , through an ignited tube. It boils at  $170^\circ$ , and is oxidized to nicotinic acid.

Conyrrine,  $C_8H_{11}N$ , is produced on heating conine hydrochloride ( $C_8H_{17}N$ ) with zinc dust. It is a bright blue, fluorescent oil, boiling at  $166$ – $168^\circ$ . It is probably the active  $\alpha$ -isopropyl pyridine, because, if oxidized, it yields picolinic acid. Heated with hydriodic acid it again forms conine (*Ber.*, 17, 826).

**Phenyl Pyridines**,  $C_5H_4(C_6H_5)N$ .

$\alpha$ - and  $\beta$ -Phenyl pyridine have been obtained from  $\alpha$ - and  $\beta$ -naphtho-quinol-

line (p. 675). By the oxidation of the latter we get  $\alpha$ - and  $\beta$ -phenyl pyridine-dicarboxylic acid,  $C_5H_3N \begin{Bmatrix} C_6H_4 \cdot CO_2H \\ CO_2H \end{Bmatrix}$ , and when  $2CO_2$  split off from these the phenyl pyridines are produced (p. 661) (*Ber.*, 16, 2306).

$\alpha$ -Phenyl pyridine boils at  $268-270^\circ$ , and when oxidized with chromic acid yields picolinic acid;  $\beta$ -phenyl pyridine boils at  $270^\circ$ , and yields nicotinic acid.

$\gamma$ -Phenyl pyridine, formed from aceto-acetic ester, etc. (p. 430), boils at  $275^\circ$ , and yields isonicotinic acid by oxidation (*Ber.*, 17, 1519).

### *Pyridine Carboxyl Compounds.*

The pyridine carboxylic acids are obtained from the homologous pyridines by oxidizing them with potassium permanganate, and are also formed by oxidizing the quinolines and alkaloids (with nitric acid, chromic acid or  $MnO_4K$ ). The lower acids can be prepared from the polycarboxylic acids, *e. g.*,  $C_5(CH_2)_3N(CO_2H)_2$  and  $C_5N(CO_2H)_5$  by the partial elimination of single carboxyls, and by completely removing the latter (by heating with lime) all the acids afford pyridine or its homologues. As these acids represent combinations of carboxyl with the basic pyridine radical, they therein manifest a deportment analogous to that of the amido-acids, and are also capable of forming salts with acids. The acid character of these acids diminishes with the increase in number of carboxyls, and disappears entirely in the penta-carboxylic acid.

*Pyridine-mono-carboxylic Acids*,  $C_5H_5NO_2 = C_5H_4N(CO_2H)$ .

All three possible isomerides are known (p. 659).

$\alpha$ -Pyridine-carboxylic Acid (1 or ortho), Picolinic acid, was first obtained by the oxidation of  $\alpha$ -picoline. It is very readily soluble in alcohol and water, crystallizes in white needles, which melt at  $135-136^\circ$ , and sublime. Ferrous sulphate imparts a faint yellow color to their solutions. By the action of  $HgNa$ , ammonia is split off, and the acid,  $C_6H_8O_3$  (oxysorbic acid?) formed; this melts at  $85^\circ$ .

$\beta$ -Pyridine-carboxylic Acid (2 or meta), Nicotinic acid, was first obtained by oxidizing nicotine. It is also prepared from  $\beta$ -methyl and ethyl pyridine, from  $\beta$ -cyanpyridine and from the three pyridine dicarboxylic acids (quinolic, cinchomeronic and isocinchomeronic acids) by the elimination of a  $CO_2$ -group. It crystallizes from hot water in needles or warty masses, and melts at  $228-229^\circ$ .

$\gamma$ -Pyridine carboxylic Acid (3 or para), Isonicotinic Acid, is obtained from the di-carboxylic acids, cinchomeronic and lutidinic acids, by the splitting-off of  $CO_2$ . It is almost insoluble in hot alcohol, forms fine needles, when crystallized from hot water, and sublimes in small plates without previous melting. When heated in a closed tube it melts at  $309^\circ$  ( $299^\circ$ ).

### *Oxypyridine-Monocarboxylic Acids.*

Various Oxypyridine Carboxylic Acids,  $C_5H_3(OH)N(CO_2H)$ , have been obtained, partly in a synthetic manner (from comanic acid,  $C_6H_4O_4$ , on digesting with ammonia), and partly from oxypyridine-dicarboxylic acids by the splitting-off of  $CO_2$  (*Ber.*, 17, 589). Dioxypyridine Carboxylic Acid,  $C_5H_2(OH)_2N(CO_2H)$ , Comenamic acid, has been prepared from comenic acid,  $C_6H_4O_5$ , on boiling with ammonium hydroxide. At  $270^\circ$  it decomposes into  $CO_2$  and dioxypyridine (p. 662).

*Methyl Pyridine Monocarboxylic Acids.*

**Picoline Carboxylic Acid**,  $C_5H_3(CH_3)N(CO_2H)$ , is obtained on heating uvitonic acid (p. 666), to  $280^\circ$ . It sublimes without previously fusing, and when oxidized becomes pyridine-dicarboxylic acid (6).

**$\beta\gamma$ -Methyl-Pyridine-Carboxylic Acid**, ( $CH_3$  in  $\gamma$ ), results on heating methyl quinolic acid to  $170^\circ$ , or when it is boiled with glacial acetic acid. It melts at  $209-210^\circ$ , and is oxidized to cinchomeronic acid.

*Pyridine Dicarboxylic Acids*,  $C_5H_5NO_4 = C_5H_3N(CO_2H)_2$ .

We are acquainted with the following of the six possible isomerides (p. 661):

1. **Quinolic Acid** ( $\alpha\beta$  or 1, 2) is obtained from quinoline and from 1 and 4 methyl quinoline by oxidation with potassium permanganate. It is difficultly soluble in alcohol, crystallizes in shining, short prisms, melts at  $222-225^\circ$ , and decomposes (by slowly heating to  $160^\circ$ ) into  $CO_2$  and nicotinic acid. Ferrous sulphate imparts a reddish-yellow color to its solution.

2. **Cinchomeronic Acid** ( $\beta\gamma$  or 2, 3) is obtained from quinine, cinchonine and cinchonidine, by oxidation with nitric acid and by the oxidation of  $\beta\gamma$ -methyl-pyridine carboxylic acid with  $MnO_4K$ . It also results from pyridine tricarboxylic acid and from apophyllenic acid. It crystallizes from water in prisms containing hydrochloric acid, and melts at  $258-259^\circ$  with decomposition into  $CO_2$ ,  $\gamma$ -pyridine carboxylic acid and a little nicotinic acid. Sodium amalgam decomposes it into  $NH_3$  and cinchonic acid,  $C_7H_6O_5$ , which breaks up into  $CO_2$  and dimethyl-fumaric anhydride (p. 338) on application of heat.

Cotarnine,  $C_{12}H_{13}NO_3$ , boiled with nitric acid, yields **Apophyllenic Acid**,  $C_8H_7NO_4$ . This is methylated cinchomeronic acid, in which the methyl group is attached to the nitrogen atom, and has the formula,  $C_5H_3(CO_2H)N(CH_3)\begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix}$

(comp. betaine, p. 265). It melts with decomposition at  $242^\circ$ , and when heated to  $250^\circ$  with hydrochloric acid decomposes into methyl chloride and cinchomeronic acid.

3. **Lutidinic Acid** ( $\alpha\gamma$  or 1, 3) is produced together with isocinchomeronic acid by oxidizing lutidine (p. 663) with potassium permanganate. It crystallizes with a molecule of water in microscopic needles, receives a blood-red color from ferrous sulphate, melts at  $219^\circ$ , and breaks up into  $CO_2$  and  $\gamma$ -pyridine carboxylic acid.

4. **Isocinchomeronic Acid** ( $\beta\alpha'$ ?). Produced together with the preceding acid, it crystallizes from acidulated hot water, with one or one and a half molecules of water, in microscopic leaflets, which melt at  $236^\circ$ , and beyond decompose into  $CO_2$  and nicotinic acid. Ferrous sulphate imparts a reddish-yellow color to the solution.

5. **Beronic Acid** is obtained from berberonic acid (p. 666) when it is heated to  $140^\circ$  with glacial acetic acid. It consists of fine needles, is not colored by ferrous sulphate, and melts at  $263^\circ$ .

6. The **pyridine dicarboxylic acid**, obtained by oxidizing picoline-carboxylic acid, appears to be identical with cinchomeronic acid.

*Oxypyridine Dicarboxylic Acids*,  $C_5H_2(OH)N(CO_2H)_2$ .

**Oxyquinolic Acid** (OH in  $\alpha'$ ), obtained by fusing quinolic acid with KOH (*Ber.*, 16, 2158), consists of thick crystals, which char at  $254^\circ$ , but do not melt. When heated to  $195^\circ$  with water it decomposes into  $CO_2$  and oxypyridine carboxylic acid (see above); the silver salt yields  $\alpha$ -oxy-pyridine when heated (*Ber.*, 17, 592).

**Ammon-chelidonic Acid**, formed from chelidonic acid with ammonia (p. 368), is resolved into  $2CO_2$  and  $\gamma$ -oxypyridine when heated to  $195^\circ$  with water (p. 662).



*Picoline Dicarboxylic Acids*,  $C_5H_2(CH_3)N(CO_2H)_2$ .

1. **Methyl-quinolic Acid** ( $\alpha, \beta, \gamma-CH_3$  in  $\gamma$ ) is produced on oxidizing  $\gamma$ -methyl-quinoline with potassium permanganate, as an intermediate product to the tricarboxylic acid. It crystallizes from water in plates or prisms, is colored yellow by ferrous sulphate, melts about  $186^\circ$  with decomposition, and yields (even on boiling with glacial acetic acid)  $CO_2$  and  $\beta\gamma$ -methylpyridine carboxylic acid (p. 665).

2. **Uvitic Acid** is formed when ammonia acts upon pyrrolic acid, consists of microscopic leaflets, is colored violet-red by ferrous sulphate, melts at  $244^\circ$ , and above  $280^\circ$  decomposes into  $CO_2$  and picoline-carboxylic acid.

3. **Picoline-dicarboxylic Acid** is obtained by heating aldehydine (p. 663) with chromic acid. It crystallizes in fine prisms, is colored reddish-yellow by ferrous sulphate, and readily sublimes without melting.

**Trimethylpyridine Dicarboxylic Acid**,  $C_5(CH_3)_3N(CO_2H)_2$ , **Collidine** dicarboxylic acid. The dimethyl ester is prepared by the oxidation of hydrocollidine dicarboxylic ester (from aceto-acetic ester with aldehyde ammonia, p. 660) in alcoholic solution with nitrous acid. The free acid, obtained by saponifying the ester, crystallizes in little needles, and decomposes when strongly heated without melting. Distilled with lime it affords a trimethyl pyridine (p. 663). By successively oxidizing its methyl groups with potassium permanganate we obtain: **lutidine tricarboxylic acid**,  $C_5(CH_3)_2N(CO_2H)_3$ , **picoline tetracarboxylic acid**,  $C_5(CH_3)N(CO_2H)_4$ , and **pyridine pentacarboxylic acid**,  $C_5N(CO_2H)_5$ . The separation of but one carboxyl from collidine-dicarboxylic acid yields collidine-monocarboxylic acid,  $C_5H(CH_3)_3N(CO_2H)$  (*Ann.*, 225, 133), which by successive oxidation affords **lutidine-dicarboxylic acid**,  $C_5H(CH_3)_2N(CO_2H)_2$ , **picoline-tricarboxylic acid**,  $C_5H(CH_3)N(CO_2H)_3$ , and **pyridine-tetracarboxylic acid**,  $C_5HN(CO_2H)_4$ .

*Pyridine Tricarboxylic Acids*,  $C_5H_3NO_6 = C_5H_2N(CO_2H)_3$ .

1.  **$\alpha\beta\gamma$ -Pyridine Tricarboxylic Acid** is obtained by completely oxidizing quinine, cinchonine, quinidine and cinchonidine, with  $MnO_4K$ , and by the same treatment of  $\gamma$ -methyl quinoline, methyl-quinolic acid (see above) and cinchoninic acid (p. 673). It is very soluble in hot water, crystallizes in plates with  $1\frac{1}{2}$  molecules  $H_2O$ , becomes anhydrous at  $115-120^\circ$ , chars and melts when rapidly heated at  $249-250^\circ$ , with decomposition. At  $180^\circ$  already it gradually breaks up (more readily on boiling with glacial acetic acid) into  $CO_2$  and cinchomeronic acid. Ferrous sulphate gives it a faint red color.

2.  **$\alpha\beta\delta$ -Pyridine Tricarboxylic Acid** is obtained, from  $\beta$ -quinoline-carboxylic acid by oxidation with  $MnO_4K$ , is colored reddish-yellow by ferrous sulphate, and softens with liberation of  $CO_2$ , about  $150^\circ$  (*Ber.*, 16, 1615).

3. **Berberonic Acid**, formed from the alkaloid berberine by oxidation with nitric acid, crystallizes with  $2H_2O$  in prisms, and melts at  $243^\circ$ . Ferrous sulphate colors it blood-red. By elimination of  $CO_2$  it yields beronic acid (p. 665), nicotinic and isonicotinic acids.

4. **Tricarbo-pyridic Acid**, from uvitonic acid (see above) and aniluvitonic acid (p. 674), by oxidation, crystallizes with  $2\frac{1}{2}$   $H_2O$  in plates or needles, melts at  $244^\circ$ , with decomposition, and is colored reddish violet by ferrous sulphate.

**Pyridine Tetracarboxylic Acid**,  $C_5NH(CO_2H)_4$ , from collidine mono-carboxylic acid (see above), crystallizes in microscopical needles, with  $2H_2O$ , is very soluble in water, is colored dark-red by ferrous sulphate and decomposes on heating without melting.

Two **Dipyridyl Dicarboxylic Acids**,  $C_5H_3N.CO_2H$ , have been obtained from the two phenanthrolines (p. 675), by oxidation with  $MnO_4K$ , and yield two dipyridyls (p. 662), by elimination of  $2CO_2$ .

## 2. QUINOLINE GROUP— $C_nH_{2n-11}N$ .

### QUINOLINE, $C_9H_7N$ .

Lepidine,  $C_{10}H_9N = C_9H_6(CH_3)N$ —Methyl quinoline.

Cryptidine,  $C_{11}H_{11}N = C_9H_5(CH_3)_2N$ —Dimethyl quinoline, etc.

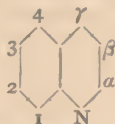
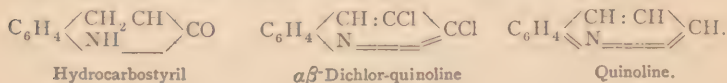
The quinoline bases occur with those of pyridine in bone-oil (p. 660), and are also obtained by distilling alkaloids (quinine, cinchonine, strychnine) with potassium hydroxide. The compounds *leucoline*,  $C_9H_7N$ , *iridoline*,  $C_{10}H_9N$ , etc., separated from coal-tar are identical with the quinoline bases (*Ber.*, 16, 1847).

As regards synthetic methods and isomerides, quinoline is a naphthalene in which a  $CH$ -group is replaced by  $N$  (p. 659) (Körner).

This was first shown by synthesizing quinoline from allyl aniline (p. 439), by passing the latter over ignited lead oxide. This is perfectly analogous to the synthesis of indol from ethyl-aniline (p. 590), and of naphthalene from phenyl butylene (p. 645) (Königs):—



Quinoline is also produced in the distillation of acrolein-aniline (p. 439). A more direct proof of the constitution of quinoline was then effected through its formation from hydrocarbostyryl (p. 544);  $PCl_5$  converts the latter into a dichloride, which upon heating with hydriodic acid yields quinoline (just as isatin affords indigo, p. 595) (A. Baeyer):—



Here, as with naphthalene and pyridine, we represent the three replaceable hydrogen atoms of the pyridine nucleus by  $\alpha$ ,  $\beta$  and  $\gamma$ ;

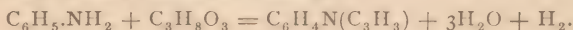
those of the benzene nucleus with 1, 2, 3 and 4. The positions 1, 2, 3 correspond to the ortho-, meta-, and para-positions of the benzene derivatives. 4 corresponds to the second *meta* position (referred to N). It is probable that the known so-called *meta derivatives* do occupy 4.

Of the great number of new synthetic methods of preparing quinoline and its derivatives, the following are the most important :

1. The condensation of the ortho-amido-compounds of such benzene derivatives, as have an oxygen atom attached to the third carbon atom of the side-chain (p. 541) (A. Baeyer).

In this way we obtain quinoline from ortho-amido-cinnamic aldehyde,  $\alpha$ -methyl-quinoline from ortho-amido-cinnamic ketone, and  $\alpha$ -oxy-quinoline from ortho-amido-cinnamic acid (p. 517). Further, ortho amido-benzyl acetone yields  $\alpha$ -methyl-hydro-quinoline (p. 527), ortho-amido-phenyl valeric acid,  $\beta$ -ethyl hydrocarbostyryl (p. 581), and from these compounds the normal quinoline derivatives— $\alpha$ -methyl quinoline and  $\beta$ -ethyl quinoline—can be obtained by the withdrawal of 2H or O.

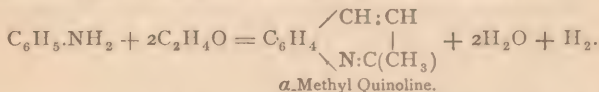
2. The production of quinoline and its derivatives by heating aniline (or amido-benzene compounds) with glycerol and sulphuric acid to about 190°. This method is of universal application and can be very readily executed (Skraup) :—



It is very probable that acrolein first results, this then combines with the aniline derivative yielding acrolein-aniline (see above), which is oxidized to the quinoline derivative by the elimination of two hydrogen atoms by sulphuric acid. Hence, the reaction proceeds more easily and rapidly by using a *mixture of aniline with nitrobenzene*, which only oxidizes. Similarly, from the three toluidines (and nitrotoluenes) we obtain the three methylquinolines (toluquinolines),  $\text{C}_{10}\text{H}_9\text{N} = \text{C}_6\text{H}_3(\text{CH}_3)\text{N}(\text{C}_3\text{H}_3)$ , from the naphthylamines (and nitronaphthalenes) the naphthoquinolines,  $\text{C}_{13}\text{H}_9\text{N}$ , and from the diamidobenzenes (and dinitrobenzenes) the phenanthrolines (p. 675). It is not necessary to apply the corresponding nitro-compounds together with the amido-derivatives; nitro-benzene mostly suffices as an oxidizing agent (*Ber.*, 17, 188).

Likewise, the chlor-, brom-, and nitro-quinolines result from the corresponding aniline derivatives. From the amido-sulphonic acids arise the quinoline sulphonic acids; from the amido-benzoic acids quinoline carboxylic acids; from the amido-phenols oxyquinolines, etc.

3. An analogous reaction is the condensation of anilines with paraldehyde, aided by  $\text{SO}_4\text{H}_2$  or HCl. Here  $\alpha$ -methyl quinolines (quinaldines) are produced (Doebner and v. Miller) :—

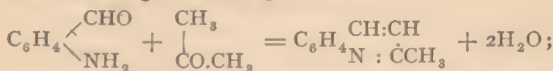


Aldol very probably is the first product. Methylene glycol and lactic acid (*Ber.*, 16, 2464) react like aldehyde. Methylated quinaldines ( $\text{C}_6\text{H}_3(\text{CH}_3)\text{N}$ ) ( $\text{C}_3\text{H}_2\cdot\text{CH}_3$ ) (*Ber.*, 16, 2469) also arise from the toluidines in the benzene nucleus

and quinaldine-carboxylic acids ( $\text{CO}_2\text{H}$  in the benzene nucleus) from the amido-benzoic acids (*Ber.*, 17, 938), etc.

4. The direct condensation of ortho-amido-benzaldehyde with aldehydes and ketones (by the action of caustic soda). The ortho-amido-derivatives of the unsaturated homologous benzaldehydes and ketones are the first products. These immediately give up water (see p. 591) (Friedländer).

Thus with acetone we get  $\alpha$ -methyl-quinoline:—



with acetophenone,  $\text{CH}_3\text{CO.C}_6\text{H}_5$ ,  $\alpha$ -phenyl quinoline; with phenyl-ethyl aldehyde,  $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ ,  $\beta$ -phenyl quinoline; with aceto-acetic ester,  $\alpha$ -methyl quinoline- $\beta$ -carboxylic acid (*Ber.*, 16, 1833); with malonic ester  $\alpha$ -oxyquinoline- $\beta$ -carboxylic acid (*Ber.*, 17, 456).

5. The condensation of aniline aceto-acetic acid (phenyl-imido-butyric acid) in which we get  $\gamma$ -oxyquinaldine,  $\text{C}_6\text{H}_4 \begin{array}{c} \swarrow \text{C(OH):CH} \\ \searrow \text{N} = \dot{\text{C}}\text{CH}_3 \end{array}$  (p. 443).

6. The condensation of malonanilic acid with  $\text{PCl}_5$ , when trichlorquinoline is produced (p. 443).

The quinoline bases are liquids which are difficultly soluble in water, alcohol and ether, and possess a penetrating odor. They are not readily attacked by nitric or chromic acid; potassium permanganate, however, destroys the benzene nucleus in them, with production of  $\alpha\beta$ -pyridine dicarboxylic acid (quinolic acid, p. 665) or its derivatives. Aceto-ortho-amido-benzoic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \swarrow \text{CO}_2\text{H} \\ \searrow \text{NH.CO.CH}_3 \end{array}$  (p. 536), is only obtained from  $\alpha$ -methyl quinoline by potassium permanganate.

**Quinoline**,  $\text{C}_9\text{H}_7\text{N}$ , is a colorless, strongly refracting liquid, with penetrating odor, and browns when exposed to the air. It boils at  $235.6^\circ$  (bar. 700 mm.); its sp. gr. = 1.0947 at  $20^\circ$ .

In preparing quinoline, digest a mixture of 38 grams aniline, 100 grams sulphuric acid, 24 grams nitrobenzene, and 120 grams glycerol, until the reaction commences. Boil them for several hours, dilute with water, distil off the nitrobenzene in a current of aqueous vapor, supersaturate with alkali, and distil the quinoline with aqueous vapor. To purify it thoroughly convert it into the acid sulphate (*Ber.*, 14, 1002).

See *Berichte*, 14, 1769, for the reactions and physiological actions of quinoline.

Quinoline affords crystalline salts with one equivalent of acids; the characteristic bichromate,  $(\text{C}_9\text{H}_7\text{N})_2\text{Cr}_2\text{O}_7\text{H}_2$ , forms yellow needles, melting at  $165^\circ$ . With the alkyl iodides quinoline pro-



duces crystalline, yellow ammonium iodides, which may be converted into peculiar bases (ammonium hydroxides) on warming with caustic soda (*Ber.*, 17, 1953, and 15, 186).

**Cyanine** ( $C_{28}H_{35}N_2I$ ) is a blue dye, and was formerly prepared by heating quinoline-amyl iodide with potassium hydroxide. It is only produced in the presence of  $\alpha$ -methyl quinoline (*Ber.*, 16, 1501, 1847); the same is true of the red-dye (*Ber.*, 16, 1082) obtained from quinoline with benzotrichloride.

**Quinoline betaine**,  $C_9H_7N \begin{smallmatrix} \diagup CH_2 \\ O \end{smallmatrix} \diagdown CO$  (the HCl-salt), is formed from quinoline and chlor-acetic acid; the free betaine melts at  $171^\circ$ .

Nascent hydrogen (HgNa, tin and hydrochloric acid) affords **Dihydro-quinoline**,  $C_9H_9N$  (melting at  $161^\circ$ ), and liquid **Tetra-hydro-quinoline**,  $C_9H_{11}N = C_6H_4 \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \\ \diagdown NH \cdot CH_2 \end{smallmatrix}$ , boiling at  $245^\circ$  (*Ber.*, 16, 727). Both are secondary bases and afford nitrosamines and tertiary bases (with alkyl iodides). For the physiological action of tetrahydro-quinoline and methyl and ethyl tetrahydro-quinoline,  $C_9H_{10}N \cdot C_2H_5$ , so-called **Kairolin**, see *Ber.*, 16, 739.

**Diquinoline**,  $C_9H_7N \cdot C_9H_7N$ , results in the action of sodium amalgam upon quinoline, or upon heating its hydrochloride. It consists of yellow needles, melting at  $114^\circ$ . It is oxidized to a dipyridine-tetracarboxylic acid.

On heating quinoline and sodium we get  **$\alpha$ -Diquinolylin**,  $C_9H_6N \cdot C_9H_6N$ , shining leaflets and needles, melting at  $175^\circ$ . Isomeric  **$\beta$ -Diquinolylin**,  $C_{18}H_{16}N_2$ , is gotten from quinoline on heating it with benzoyl chloride and by the distillation of  $\gamma$ -quinoline carboxylic acid with lime. It consists of brilliant needles, melting at  $192^\circ$ .

The chlor-, brom-, and nitro-quinolines, with the substitutions in the benzene nucleus, are prepared synthetically by Skraup's reaction from the chlor-, brom-, and nitro-anilines.  **$\alpha$ -Chlorquinoline**,  $C_9H_6ClN$ , is obtained from  $\alpha$ -oxyquinoline with  $PCl_5$  and  $PCl_3O$ ; it affords long needles, fusing at  $38^\circ$ , and boiling at  $266^\circ$ . It is a feeble base. When heated to  $120^\circ$  with water it regenerates  $\alpha$ -oxyquinoline; alkyl ethers appear when it is acted upon by sodium alcoholates. **1-Nitroquinoline** (ortho) is prepared from ortho-nitraniline, and by the nitration of quinoline with fuming nitric acid. It melts at  $89^\circ$ , and is a strong base.

**Amido-quinolines**,  $C_9H_6(H_2N)N$  (substituted in benzene nucleus), are produced in the reduction of the nitroquinolines and upon heating the oxyquinolines,  $C_9H_6(OH)N$ , with ammonia-zinc chloride.

**1- and 4-Quinoline Sulphonic Acids** (ortho- and meta-, comp. p. 668), are formed when quinoline is heated to  $100-270^\circ$  with fuming sulphuric acid (*Ber.*, 16, 721). **3-Quinoline Sulphonic Acid** (para), is prepared synthetically from sulphanilic acid. All three are crystalline, and when fused with KOH yield corresponding oxyquinolines.

Two cyanquinolines result from the distillation of the sodium salts of 1- and 4-quinoline sulphonic acids with KCN. **1-Cyanquinoline**,  $C_9H_6(CN)N$  (ortho), is liquid and by saponification affords 1-quinoline-carboxylic acid. **4-Cyanquinoline** (meta) consists of shining needles, melting at  $88^\circ$ , and yields 4-quinoline-carboxylic acid (*Ber.*, 17, 765).

#### **Oxyquinolines**, $C_9H_6(OH)N$ .

The oxyquinolines containing the hydroxyl in the benzene nucleus, called also quinophenols (1, 4, and 3, or ortho, meta, and para, p. 667), are synthesized from the three amidophenols by Skraup's reaction. 1- and 4-oxyquinolines have also been prepared from the quinoline sulphonic acids (see above).

**1 Oxyquinoline** (ortho) is also produced from 1-chlorquinoline (see above), and is most readily prepared from 1-quinoline sulphonie acid (*Ber.*, 16, 712). It crystallizes in white needles, has the odor of saffron, melts at  $75^{\circ}$ , boils at  $258^{\circ}$ , and is volatile in steam. Tin and hydrochloric acid convert it into 1-Oxytetrahydroquinoline,  $C_9H_9(OH)NH$ . This affords shining leaflets or needles, melting at  $120^{\circ}$ . It yields oxytetrahydro methyl-quinoline,  $C_9H_9(OH)N.CH_3$ , melting at  $114^{\circ}$ , when it is acted upon by methyl iodide. The hydrochloric acid salt of this base,  $C_{10}H_{13}ON.HCl + H_2O$ , is **Kairine** (*Ber.*, 16, 720), which is applied as an *antipyretic*.

**4-Oxyquinoline** (meta), from para-amidophenol and from 4-quinoline sulphonie acid, melts at  $235-238^{\circ}$  (*Ber.*, 16, 721). It dissolves readily in alkalis and acids; the solutions show green fluorescence.

**3-Oxyquinoline** (para), from para-amidophenol, melts at  $190^{\circ}$  (*Ber.*, 15, 893). Its methyl ester,  $C_9H_8(O.CH_3)N$ , is very probably the base  $-C_{10}H_9NO$ —obtained in fusing quinine with potassium hydroxide.

The oxyquinolines with the hydroxyl in the pyridine nucleus are:—

**$\alpha$ -Oxyquinoline**,  $C_9H_8(OH)N$ , **Carbostyryl**, the lactim of ortho-amido-cinnamic acid (p. 541 and p. 580), which is most readily obtained by digesting ortho-nitro-cinnamic ester with alcoholic ammonium sulphide (*Ber.*, 14, 1916).  $CO_2$  precipitates it, in white needles, from its alkaline solution. It crystallizes from hot water in fine needles, from alcohol in large prisms. It melts at  $198-199^{\circ}$  and sublimes. Excess of alkali precipitates the alkali salts in the form of brilliant leaflets. When oxidized with  $KMnO_4$  it becomes oxalylanthranilic acid (p. 536).

The alkyl ethers of carbostyryl are produced when the latter is boiled with alkyl iodides, KOH and alcohol, or from  $\alpha$  chlorquinoline (p. 670), with alcoholic KOH, and from ortho-amido-cinnamic ester when it is digested with alcoholic  $ZnCl_2$  (p. 580). They are oils with aromatic odor, are volatile in aqueous vapor and saponified when heated with hydrochloric acid. (Distinction from the isomeric lactam ethers, pp. 541 and 544). **Methyl carbostyryl** boils at  $247^{\circ}$ , **ethyl carbostyryl** at  $256^{\circ}$ .

**Kynurine**,  $C_9H_8(OH)N + 3H_2O$ , is an oxyquinoline, obtained from oxyquinoline-carboxylic acid. When anhydrous it melts at  $201^{\circ}$ , and heated with zinc dust forms quinoline, and with  $MnO_4K$  it is oxidized to oxalylanthranilic acid (kynuric acid, p. 536).

Different *dioxiquinolines*,  $C_9H_5(OH)_2N$ , oxycarbostyryls, have been obtained from the chlorcarbostyryls, etc., *Ber.*, 15, 2153 and 2681).

The formation of  $\gamma$ -oxycarbostyryl from ortho-amido phenyl-propionic acid (p. 582), is worthy of note.

### Quinoline Homologues.

The methylated quinolines, the *Toluquinolines*, containing the substituted groups in the benzene nucleus, have been obtained by Skraup's reaction from the three toluidines. All three (by destruction of the benzene nucleus) yield quinolic acid (p. 665), when oxidized with  $MnO_4K$ .

**1-Methyl-quinoline** (ortho), from ortho-toluidine, boils at  $248^{\circ}$ . **4-Methyl-quinoline** (meta) boils at  $260^{\circ}$ . **3-Methyl-quinoline** (para), at  $258^{\circ}$ .

**$\alpha$ -Methyl-quinoline**,  $C_9H_8(CH_3)N$ , **Quinaldine**, was first obtained on heating aniline with aldehyde and sulphuric acid (p. 668).

It is also formed in the condensation of ortho-amido-benzaldehyde with acetone when warmed with sodium hydroxide (p. 669); by the reduction of ortho-nitrobenzal acetone (p. 575); from ortho-nitro-cinnamyl-aceto-acetic ester (*Ber.*, 16, 165); and from  $\gamma$ -oxy-quinaldine (from anil-aceto-acetic acid, p. 669), etc.

The most advantageous course to procure it consists in digesting 1 part of aniline with  $1\frac{1}{2}$  parts of paraldehyde and 2 parts common hydrochloric acid, and then distil the product with sodium (*Ber.*, 16, 2465). As much as 25 per cent. quinoline is found in coal-tar, but it cannot be isolated from it (*Ber.*, 16, 1082).

Quinaldine is a liquid with a faint odor resembling that of quinoline, and boils at  $238-239^\circ$ . When  $\text{MnO}_4\text{K}$  acts on it, the pyridine ring is broken and acetyl-anthranilic acid (p. 536), results. Chromic acid oxidizes it to  $\alpha$ -quinoline carboxylic acid (p. 673), and nitric acid to nitro- $\alpha$  quinoline carboxylic acid.

Quinaldine condenses with benzaldehyde or benzal-chloride (when heated with  $\text{ZnCl}_2$ ) to **Benzylidene-quinaldine**,  $\text{C}_9\text{H}_6\text{N}:\text{CH}:\text{CH}.\text{C}_6\text{H}_5$ , melting at  $100^\circ$ . With phthalic anhydride it yields **quinophthalone** (quinoline yellow),  $\text{C}_9\text{H}_6\text{N}.\text{CH}(\text{CO})\text{C}_6\text{H}_4$  (p. 548); this sublimes in yellow needles, melts at  $235^\circ$ , and imparts a beautiful yellow to silk and wool (*Ber.*, 16, 2602).

Quinaldine (lepidine) combines with alkyl iodides (chlorides), forming ammonium iodides, which when mixed with a quinoline-alkyl iodide (p. 670), and heated with KOH pass into peculiar red and blue dyes—the so-called *Cyanines* (*Ber.*, 16, 1501, 1847):—



**Tetrahydro-quinaldine**,  $\text{C}_{10}\text{H}_{13}\text{N}$ , is formed from quinaldine with tin and hydrochloric acid, also by reduction of ortho-nitro benzoyl-acetone (p. 524). It boils at  $247^\circ$ , and becomes blood-red in color when oxidized.

$\gamma$ -Oxyquinaldine,  $\text{C}_9\text{H}_5(\text{CH}_3)(\text{OH})\text{N}$ , from anilo-aceto-acetic acid (p. 669), boils at  $222^\circ$ . The condensation of ortho- and para-toluidine with aceto-acetic ester gives rise to methylated  $\gamma$ -oxy-quinaldines,  $\text{C}_9\text{H}_4(\text{CH}_3)_2(\text{OH})\text{N}$  (*Ber.*, 17, 542).

$\gamma$ -**Methyl-quinoline**,  $\text{C}_9\text{H}_6(\text{CH}_3)\text{N}$ , **Lepidine**, is obtained on distilling cinchonine with calcium oxide, or better, with lead oxide (*Ber.*, 16, 1381). It possesses an odor like that of quinoline, and boils at  $256-258^\circ$ . Chromic acid oxidizes it to  $\gamma$ -quinoline-carboxylic acid.  $\text{MnO}_4\text{K}$  first produces methyl-pyridine-dicarboxylic acid (methylquinolic acid, p. 666), and afterwards pyridine-tricarboxylic acid ( $\alpha,\beta,\gamma$ ). **Iridoline**, obtained from coal-tar, appears to be identical with quinoline.

**Dimethyl quinolines**,  $\text{C}_9\text{H}_5(\text{CH}_3)_2\text{N}$ , quinaldines containing the methyl in the benzene nucleus, have been obtained by the condensation of three toluidines with paraldehyde (p. 668). The **Dimethyl-quinoline** (2, 3 or 3, 4), resulting from ortho-xylidine with glycerol, etc., boils at  $264^\circ$  (*Ber.*, 17, 1489).

$\beta$ -**Ethyl quinoline**,  $\text{C}_9\text{H}_6(\text{C}_2\text{H}_5)\text{N}$ , is formed by reducing  $\beta$ -ethylhydrocarbostyryl (p. 581), similar to quinoline from hydro-carbo styryl (p. 667) (*Ber.*, 13, 120).

**$\alpha$ -Acetylquinoline**,  $C_9H_6(CH_2.CO.CH_3)N$ , is obtained by reducing o-nitrocinnamyl-acetone (*Ber.*, 16, 163), and consists of golden yellow needles, melting at  $76^\circ$ . Heated with hydrochloric acid it passes into quinaldine.

**3-Phenylquinoline** (para),  $C_9H_6(C_6H_5)N$ , formed from paramido-diphenyl,  $C_6H_5.C_6H_4.NH_2$ , with glycerol, etc., consists of plates, and melts at  $109^\circ$ .

**4-Phenylquinoline**,  $C_9H_6(C_6H_5)N$ , is obtained from cinnamic aldehyde and aniline upon heating them with hydrochloric acid (*Ber.*, 16, 1664); also by the condensation of ortho-amido-benzaldehyde with acetophenone by means of sodium hydroxide (p. 669). It consists of brilliant needles, melting at  $84^\circ$ .

**$\beta$ -Phenylquinoline**,  $C_9H_6(C_6H_5)N$ , is produced in the condensation of ortho-amido-benzaldehyde with phenyl-acetaldehyde. It is an oil, which solidifies on cooling.

Upon heating acetanilide,  $C_6H_5.NH.CO.CH_3$ , with  $ZnCl_2$  to  $270^\circ$  (by condensation of 2 molecules of the ortho-amido-acetophenone which is produced first), we obtain **Flavaniline**,  $C_{16}H_{14}N_2$ , applied as a beautiful yellow dye (*Ber.*, 15, 1500). It is  **$\alpha$ -Amido-phenyl- $\gamma$ -methylquinoline**,  $C_9H_5(C_6H_4.NH_2)(CH_3)N$ . Nitrous acid converts it into so-called **Flavenol** =  **$\alpha$ -Oxyphenyl- $\gamma$ -methylquinoline**,  $C_9H_5(C_6H_4.OH)(CH_3)N$ , which when heated with zinc dust becomes **Flavoline** =  **$\alpha$ -Phenyl- $\gamma$ -methylquinoline**,  $C_9H_5(C_6H_5)(CH_3)N$ . Potassium permanganate oxidizes flavenol to methylquinoline-carboxylic acid (p. 674), and then to methyl pyridine tricarboxylic acid.

#### *Quinoline Carboxylic Acids.*

The quinoline carboxylic acids,  $C_9H_6N.CO_2H$ , contain carboxyl in the benzene nucleus or the quinoline benz-carboxylic acids are obtained from the three amido-benzoic acids with glycerol, etc.

**1-Quinoline Carboxylic Acid**,  $C_9H_6N(CO_2H)$  (ortho), is formed by saponifying 1-cyanquinoline, consists of needles like those of benzoic acid, melts at  $187^\circ$ , and sublimes. **4-Quinoline Carboxylic Acid** (meta), from meta-amido-carboxylic acid and meta-cyanquinoline, sublimes as a crystalline powder or in flakes, is almost insoluble in water and melts at  $320^\circ$ . **3-Quinoline Carboxylic Acid** (para) is a crystalline powder, difficultly soluble in water, and melts at  $291^\circ$  with charring. Quinoline results from all three acids when they are distilled with lime.

**$\alpha$ -Quinoline Carboxylic Acid**,  $C_9H_6N(CO_2H)$ , **Quinaldic Acid**, is obtained in oxidizing quinaldine with chromic acid. It crystallizes from hot water in needles containing  $2H_2O$ ; it effloresces in the air, melts at  $156^\circ$ , and further decomposes into  $CO_2$  and quinoline.

**$\beta$ -Quinoline Carboxylic Acid** is produced on oxidizing  $\beta$ -ethylquinoline with chromic acid, and by heating *Acridic acid* to  $130^\circ$ . It crystallizes in small plates, melts at  $171^\circ$ , and when oxidized with  $MnO_4K$  yields  $\alpha,\beta,\beta'$ -pyridine tricarboxylic acid (p. 666) (*Ber.*, 16, 1610).

**$\gamma$ -Quinoline Carboxylic Acid**,  $C_9H_6N(CO_2H)$ , **Cinchoninic Acid**, is produced in oxidizing cinchonine and cinchonidine with  $MnO_4K$ , or  $\gamma$ -methylquinoline with chromic acid. It crystallizes in needles, containing  $1H_2O$ , in thick prisms and plates with  $2H_2O$ , loses water at  $100^\circ$ , softens at  $235^\circ$ , and melts at  $254^\circ$ . When dis-



tilled with lime it affords quinoline;  $\text{MnO}_4\text{K}$  oxidizes it to  $\alpha,\beta,\gamma$ -pyridine tricarboxylic acid.

By heating cinchoninic acid with  $\text{SO}_4\text{H}_2$  and  $\text{P}_2\text{O}_5$  we obtain 1- and 3- *Sulphoacids*,  $\text{C}_9\text{H}_5(\text{SO}_3\text{H})\text{N}(\text{CO}_2\text{H})$  (ortho and para), which, on fusion with potash yield 1- and 3-oxy-cinchoninic acids,  $\text{C}_9\text{H}_5(\text{OH})\text{N}(\text{CO}_2\text{H})$ . The former melts at  $255^\circ$ , and if distilled with lime yields  $\text{CO}_2$  and 1-oxy-quinoline (ortho); the latter melts at  $320^\circ$ , and yields 3-oxyquinoline (para) (*Ber.*, 14, 2282).

The so-called **Quininic Acid**,  $\text{C}_9\text{H}_5(\text{O}.\text{CH}_3)\text{N}(\text{CO}_2\text{H})$  ( $\alpha, \gamma$ ), is the phenol-ester of 3-oxy-cinchoninic or **Xantho-quinic acid**. It is obtained by oxidizing quinine sulphate with chromic acid; crystallizes in long, yellow prisms, dissolves in alcohol with a blue fluorescence, and melts at  $280^\circ$ . When heated to  $230^\circ$  with hydrochloric acid it decomposes into methyl chloride and 3-oxy-cinchoninic acid.

**$\alpha$ -Oxy-cinchoninic Acid**,  $\text{C}_9\text{H}_5(\text{OH})\text{N}(\text{CO}_2\text{H})$  ( $\alpha, \gamma$ ), carbostyryl- $\gamma$ -carboxylic acid, is formed on melting cinchoninic acid with potash, consists of fine needles, and melts at  $310^\circ$ . It decomposes into  $\text{CO}_2$  and carbostyryl (*Ber.*, 16, 2152), if its silver salt be distilled.

**$\alpha$ -Oxy  $\beta$ -quinoline Carboxylic Acid**,  $\text{C}_9\text{H}_5(\text{OH})\text{N}(\text{CO}_2\text{H})$  ( $\alpha, \beta$ ), **Carbostyryl- $\beta$ -carboxylic Acid**, results in the condensation of ortho-amido benzaldehyde with malonic acid (p. 669), melts above  $320^\circ$ , is colored reddish-brown by ferric chloride, and on heating its silver salt yields  $\text{CO}_2$  and carbostyryl.

**Kynurenic Acid**,  $\text{C}_9\text{H}_5(\text{OH})\text{N}(\text{CO}_2\text{H})$ , is also an oxy-quinoline carboxylic acid. It occurs in the urine of dogs. It consists of needles containing  $\text{H}_2\text{O}$ , becomes anhydrous at  $140^\circ$ , and melts at  $257^\circ$ . Fusion with  $\text{KOH}$  converts it into  $\text{CO}_2$  and kynurine (p. 671).

The **Quinaldine Carboxylic Acids** (quinaldines with carboxyl in the benzene nucleus),  **$\alpha$ -Methyl quinoline-carboxylic acids** (ortho, meta and para), are produced by the condensation of the three amido-benzoic acids with aldehyde (p. 668).

**Aniluvitonic Acid**,  $\text{C}_{11}\text{H}_9\text{NO}_2$ , belongs to this class of acids. It forms on boiling anilpyro-racemic acid (p. 443). It melts at  $142^\circ$ , and when distilled with lime yields methyl quinoline.

**$\alpha$ -Methyl quinoline- $\beta$ -carboxylic Acid**,  $\text{C}_9\text{H}_5\text{N}(\text{CH}_3).\text{CO}_2\text{H}$ . The ethyl ester results from the condensation of ortho-amido-benzaldehyde with aceto-acetic esters (p. 669), melts about  $71^\circ$ , and affords the free acid by saponification; this melts at  $234^\circ$ .

**$\gamma$ -Methyl quinoline- $\alpha$ -carboxylic Acid**,  $\text{C}_9\text{H}_5\text{N}(\text{CH}_3).\text{CO}_2\text{H}$ , is obtained by oxidizing flavenol (p. 673), and melts at  $182^\circ$ , with decomposition into  $\text{CO}_2$  and  $\gamma$ -methyl quinoline (?).

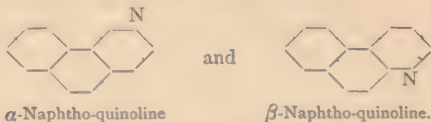
**$\alpha,\beta$ -Quinoline-dicarboxylic Acid**,  $\text{C}_9\text{H}_5\text{N}(\text{CO}_2\text{H})_2$ , **Acridic Acid**, is produced when acridine is oxidized with potassium permanganate, crystallizes in needles or plates, and decomposes at  $120$ – $130^\circ$  into  $\text{CO}_2$  and  $\beta$ -quinoline-carboxylic acid (*Ber.*, 16, 1610).

**$\alpha,\beta,\gamma$ -Quinoline-tricarboxylic Acid**,  $\text{C}_9\text{H}_4\text{N}(\text{CO}_2\text{H})_3$ , is obtained by oxidizing methyl acridine (*Ber.*, 16, 1808).

#### Complex Quinolines.

Just as pyridine,  $\text{C}_5\text{H}_5\text{N}$ , and quinoline,  $\text{C}_9\text{H}_7\text{N}$ , are derived from benzene,  $\text{C}_6\text{H}_6$ , and naphthalene,  $\text{C}_{10}\text{H}_8$ , so do corresponding quinolines result from the higher condensed benzenes.

The so-called **Naphtho-quinolines**,  $C_{13}H_9N$ , are derived from phenanthrene by the replacement of a  $CH$ -group by nitrogen:—



They are produced when  $\alpha$ - and  $\beta$ -naphthylamines are heated with glycerol, nitrobenzene and sulphuric acid.

$\alpha$ -Naphtho-quinoline melts at  $50^\circ$ , and boils at  $251^\circ$ .  $\beta$ -Naphtho-quinoline, melts at  $90^\circ$ . When they are oxidized, they yield two ( $\alpha$ - and  $\beta$ -) phenyl-pyridine dicarboxylic acids,  $C_6H_4(CO_2H).C_5H_3N(CO_2H)$  (this is like the formation of diphenic acid from phenanthrene, p. 655), which split off  $2CO_2$  and become  $\alpha$ - and  $\beta$ -phenyl-pyridines (p. 664).

Phenanthridine is isomeric with naphthoquinoline. In it one of the intermediate  $CH$ -groups of phenanthrene is replaced by nitrogen. **Methyl Phenanthridine**,  $C_{13}H_8(CH_3)N$ , has also been obtained from benzylidine-ortho-toluidine (p. 515).

Two **Phenanthrolines**,  $C_{12}H_8N_2$ , have been prepared by heating meta- and para-diamidobenzene with glycerol, etc. These are derived from phenanthrene by replacement of 2  $CH$ -groups by 2 nitrogen-atoms (*Ber.*, 16, 2522). By oxidation they yield two dipyridyl-dicarboxylic acids (p. 667).

**Anthraquinoline**,  $C_{17}H_{13}N = C_6H_4 \begin{smallmatrix} \diagup CH \\ \diagdown CH \end{smallmatrix} C_6H_4 \begin{smallmatrix} \diagup CH:CH \\ \diagdown N:CH \end{smallmatrix}$ , is obtained from anthramine (p. 637) on heating glycerol, nitrobenzene and sulphuric acid, also by the distillation of alizarine blue with zinc dust (p. 642). It sublimes in colorless leaflets, melts at  $170^\circ$ , and boils at  $446^\circ$ . Its solutions fluoresce very intensely. By oxidation with chromic acid in glacial acetic acid, it affords a quinone corresponding to anthraquinone, whose dioxy-compound is alizarine blue.

#### Acridines.

**Acridine**,  $C_{13}H_9N$ , is derived from anthracene by replacing one intermediate  $CH$ -group by nitrogen. It is prepared synthetically by heating diphenylamine and formic acid or formyl diphenylamine  $(C_6H_5)_2N.CHO$ , with  $ZnCl_2$  (*Ber.*, 16, 1802 and 1820, *Ann.*, 224, 1):—



Homologous acridines are similarly obtained from diphenylamine and the higher fatty acids. In them the hydrogen of the  $CH$ -group is replaced by alkyls. The oxidation of acridine with potassium permanganate affords (through the destruction of a benzene nucleus)  $\alpha,\beta$ -quinoline dicarboxylic acid (p. 674).

Acridine has also been obtained from ortho-tolylaniline,  $C_6H_5.NH.C_6H_4.CH_3$ , by conducting the vapors through a red-hot tube (analogous to the synthesis of anthracene); and by heating diphenylamine with chloroform and  $ZnCl_2$  to  $200^\circ$  (*Ber.*, 17, 102). It occurs in crude anthracene and dissolves in sulphuric acid with a beautiful green fluorescence. It readily sublimes in colorless leaflets, melts at  $107^\circ$  ( $111^\circ$ ), distils above  $360^\circ$ , and has a very pungent odor.

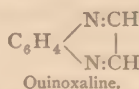
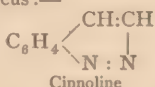
**Methyl Acridine**,  $C_{13}H_8(CH_3)N$ , from diphenylamine and acetic acid, melts at  $114^\circ$ . **Phenyl Acridine**,  $C_{13}H_8(C_6H_5)N$ , from diphenylamine and benzoic acid, melts at  $181^\circ$ , and distils above  $360^\circ$ .

The acridines yield iodides with the alcoholic iodides. Silver oxide or alkalis convert them into peculiar ammonium bases (*Ber.*, 17, 1953).

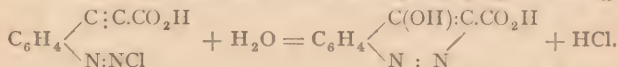
**Chrysaniline** is a diamido-phenyl-acridine,  $C_{19}H_{11}N(NH_2)_2$ . It is obtained as a by-product in the rosaniline manufacture. It affords salts with the acids (1 equivalent); these dye silk and wool a beautiful yellow—*Mandarine yellow*. Less pure it is known as *Leather yellow* (Xanthine). When mixed with a little rosaniline hydrochloride it constitutes the so-called *Phosphin*.

When chrysaniline is diazotized and boiled with alcohol (p. 458), it yields phenyl-acridine. If heated to  $180^\circ$  with hydrochloric acid, an amido-group splits off and *Chrysophenol*,  $C_{19}H_{11}(OH)N.NH_2$ , is produced. Chrysaniline has been prepared synthetically by the fusion of triamido-triphenyl methane (from ortho-nitro-benzaldehyde with aniline, p. 617) with arsenic acid (*Ber.*, 17, 208, 433).

**Cinnoline** and **Quinoxaline** are quinolines containing two nitrogen-atoms in one benzene nucleus:—



The cinnoline nucleus has been obtained by a closed ring being formed from the diazo-compounds. Thus, **Oxy-cinnoline Carboxylic Acid** (*Ber.*, 16, 677) is obtained from the diazo-chloride of ortho-amidophenyl propiolic acid (p. 582):

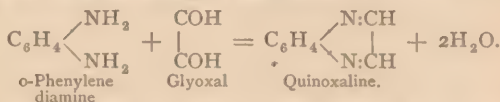


**Methyl Cinnoline-carboxylic Acid**,  $C_6H_3(CO_2H)\begin{array}{c} \text{C(CH}_3\text{):CH} \\ \diagup \quad \diagdown \\ \text{N:N} \end{array}$  (*Ber.*, 17, 724), is obtained in the same way, from the diazo-chloride of ortho-amidopropenyl benzoic acid (p. 557),  $C_6H_3(CO_2H)\begin{array}{c} \text{C(CH}_3\text{):CH}_2 \\ \diagup \quad \diagdown \\ \text{N}_2\text{Cl} \end{array}$ .

Oxycinnoline-carboxylic acid,  $C_8H_4(OH)N_2(CO_2H)$ , melts at  $260^\circ$ , with the separation of  $CO_2$  and formation of **Oxycinnoline**,  $C_8H_5(OH)N_2$ , which melts at  $225^\circ$ , and when heated with zinc dust yields cinnoline.

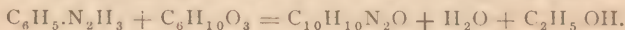
**Quinazol**,  $C_6H_4\begin{array}{c} \text{CH:CH} \\ \diagup \quad \diagdown \\ \text{NH.NH} \end{array}$ , is a dihydrocinnoline. The **ethyl quinazol-carboxylic acid**,  $C_8H_6(C_2H_5)_2N_2(CO_2H)$ , has been prepared by reducing nitroso-ortho-ethyl amido-cinnamic acid (*Ber.*, 16, 654).

The quinoxalines arise from the condensation of ortho-phenylene diamines with glyoxal diketones and analogous compounds:—



Benzil, phenanthraquinone and pyroracemic acid (*Ber.*, 17, 319) react like glyoxal.

The so-called *Oxyquinizine derivatives* contain a peculiar binding of two nitrogen atoms in the hydrogenized quinoline nucleus. They appear in the condensation of the phenyl hydrazines with the esters of aceto-acetic acid:—



The **methyl-oxy-quinizine**,  $C_{10}H_{10}N_2O$ , obtained in this way yields, by the action of methyl iodide and sodium hydroxide, **Dimethyl-oxy-quinizine**,  $C_{10}H_9N_2(CH_3)_2O$ , a base, which melts at  $113^\circ$ , dissolves readily in water, and finds application under the name of *antipyrine* (*Ber.*, 17, 2037).

## ALKALOIDS.

By this term we know all nitrogenous vegetable compounds of basic character, or their derivatives, from which bases may be isolated. Many of them (betaine, asparagine, theine), have, in accord with their constitution, been already discussed with the various amido-derivatives; the most of those remaining which have been studied recently, show themselves to be derivatives of the pyridine and quinoline bases. The latter can be easily liberated from them. Like the benzene derivatives they have much in common in their whole deportment. They constitute chiefly the active principles of the vegetable drugs employed as medicines or poisons.

Some alkaloids contain no oxygen, and then are generally liquid and volatile. Most of them do, however, contain that element, and are solid and non-volatile. Nearly all (like the pyridine and quinoline bases) are tertiary amines; some, however (hydrogen addition products of the pyridine nucleus, p. 662), belong to the secondary amines. Tannic acid, phospho-molybdic acid, platinic chloride, and many double salts (like  $HgI_2 \cdot 2KI$ ) precipitate all these bases from their aqueous solutions; iodine affords crystalline per-iodides with many of them. The bases are regained from these compounds by alkalies.

**Piperidine**,  $C_5H_{11}N$ , Hexahydropyridine,  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} NH$ , occurs combined with piperic acid (p. 588) in piperine (see below). It is obtained artificially from pyridine by means of tin and hydrochloric acid, or more readily when sodium acts on the alcoholic solution (p. 661).

The homologous piperidines, *e. g.*,  $C_5H_9(CH_3)_3NH$  (*Ber.*, 17, 389, 773), are similarly obtained from the homologous pyridines. *Vice versa*, piperidine is oxidized to pyridine by the splitting-off of six hydrogen atoms (when heated to  $300^\circ$  with sulphuric acid, or on boiling it with silver oxide). Bromine converts acetyl piperidine into pyridine and brom-pyridines (*Ber.*, 16, 588).

Piperidine is a liquid, easily soluble in water and alcohol, boils at  $106^\circ$ , and has an odor resembling that of pepper and ammonia. It reacts alkaline, and affords crystalline salts with one equivalent of the acids. Being a secondary amine the imido-hydrogen can be replaced by alkyls and acid radicals.



**n-Methyl-piperidine**,  $C_5H_{10}N.CH_3$ , and **n-Ethyl-piperidine**,  $C_5H_{10}N.C_2H_5$ , are colorless liquids; the first boils at  $107^\circ$ , the second at  $128^\circ$ . **n-Benzoyl-piperidine**,  $C_5H_{10}N.C_7H_5O$ , is a crystalline body, produced by the action of benzoyl chloride.

**Piperine**,  $C_{17}H_{27}NO_3 = C_5H_{10}N.C_{12}H_{17}O_3$ , is an analogous acid derivative of piperidine with piperic acid. It is present in the different varieties of pepper (as *Papaver niger*). It is made artificially when piperine acts on piperyl chloride. It crystallizes in prisms, and melts at  $128-129^\circ$ . It decomposes into piperidine and piperic acid when it is boiled with potassium hydroxide.

The *homologous* piperidines are produced from the homologous pyridines by the action of sodium upon their alcoholic solutions (see below).  **$\alpha$ -Propyl-piperidine**,  $C_8H_{13}(C_3H_7)NH$ , boils at  $165-168^\circ$ ,  **$\gamma$ -Propyl-piperidine** at  $157-161^\circ$ ; both are very similar to isomeric conine (*Ber.*, 17, 762).

**Tetramethyl piperidine**,  $C_5H_9(CH_3)_4NH$ , appears to be **Triacetone**, obtained from triacetoneamine (p. 166).

If **n-dimethyl-piperidine iodide**,  $C_5H_{10}N(CH_3)_2.CH_3I$  (from **n-methyl piperidine** with  $CH_3I$ ), be heated with soda, we obtain so-called **Dimethyl-piperidine**,  $C_5H_9N(CH_3)_2$ , which is also prepared on heating piperidine hydrochloride with methyl alcohol to  $200^\circ$ . Piperidine hydrochloride reunites again with methyl iodide to form an ammonium iodide, which is split into trimethylamine and **piperylene**,  $C_5H_8$ . Consult *Ber.*, 16, 2058, upon the constitution of dimethyl piperidine, and the hydrocarbon piperylene (boiling at  $42^\circ$ ) derived from it.

**Conine**,  $C_8H_{17}N = C_5H_9(C_3H_7)NH$ , is very similar to  **$\alpha$ -isopropyl-piperidine** (see above), perfectly like it in physiological action and differing almost solely in its optical activity.  **$\alpha$ -Propyl-pyridine** (p. 668), called **conyrine**, results on heating the hydrochloride with zinc dust. It regenerates conine with hydriodic acid.

Conine occurs in hemlock (*Conium maculatum*), chiefly in the seeds, and is obtained by extraction with acetic acid or distillation with soda. It is a colorless liquid, having the odor of hemlock, and boiling at  $167-168^\circ$ . It dissolves 25 per cent. of water, which it separates on warming, and becomes turbid in consequence. It is soluble in 90 parts of water. It deviates the plane of polarization to the left.

Nitric acid oxidizes conine to butyric acid, and potassium permanganate converts it into  **$\alpha$ -pyridine carboxylic acid**. When heated with hydriodic acid it yields normal octane,  $C_8H_{18}$  (*Ber.*, 16, 590).

As secondary amine it yields alkyl and acetyl derivatives. If its **Nitrosamine**,  $C_8H_{16}N(NO)$  (Azoconhydrine), be digested with  $P_2O_5$  it affords **Conylene**,  $C_8H_{14}$ , boiling at  $125^\circ$ . Dimethyl conine iodide,  $C_8H_{16}N(CH_3)_2.CH_3I$ , obtained from nitro-methyl conine and methyl-iodide, manifests the same deportment as the piperidine derivative (see above), and finally decomposes into trimethylamine and conylene.

In an alkaline bromine solution conine affords **bromamine**,  $C_8H_{16}NBr$  (p. 126), which on treatment with alkalis and acids yields two bases—a tertiary,  $C_8H_{15}N$ , and a secondary,  $C_9H_{14}NH$ —(*Ber.*, 16, 558). **Paraconine**,  $C_8H_{15}N$ , is isomeric with them. It is obtained on heating normal butyric aldehyde with ammonia (p. 157). It boils at  $168-170^\circ$ , is very similar to conine, and when oxidized affords butyric and a pyridine carboxylic acid, and therefore, must be

considered as a tetra-hydride of a propyl-pyridine,  $C_5H_8(C_3H_7)N$  (*Ber.*, 14, 2105). The bases, *Valeridine*,  $C_{10}H_{19}N$ , and *Valeritrine*,  $C_{15}H_{27}N$  (p. 158), derived from amyl aldehyde, in all probability possess an analogous constitution.

**Tropidine**,  $C_8H_{13}N$ , is analogous to conine, and para-conine and is derived from the base tropine,  $C_8H_{15}NO$  (p. 682). It is an oil, boils at  $162^\circ$ , and has the odor of conine. It decomposes into methyl bromide, ethylene bromide and dibrompyridine on heating its hydrobromic acid salt with bromine. Tropidine is therefore very probably an ethylene-methyl-tetrahydropyridine,  $C_5H_6(C_2H_4)N(CH_3)$  (*Ber.*, 15, 1142).

**Conhydrine**,  $C_8H_{17}NO$ , is intimately related to conine, occurring with the latter in hemlock and in the distillation it passes over last. It crystallizes in leaflets, melts at  $120^\circ$ , distils at  $240^\circ$ , and sublimes about  $100^\circ$ . When distilled with  $P_2O_5$  it affords a basic oil (*Ber.*, 15, 2315).

**Nicotine**,  $C_{10}H_{14}N_2$ , occurs in the leaves and seeds of tobacco plants. Ordinary tobacco contains 7–8 per cent., and Havana tobacco 2 per cent. of it. It is an oil readily soluble in water, alcohol and ether. Its sp. gr. = 1.011 at  $15^\circ$ . Its odor is very penetrating. It boils with partial decomposition at  $250^\circ$ , and in a current of hydrogen at  $150$ – $200^\circ$ , without any alteration. It is a diacidic tertiary base.  $MnO_4K$  oxidizes it to nicotinic acid. Heated with sulphur or copper it yields isodipyridine, and therefore, represents the hydride of a dipyridine (p. 662).

**Sparteine**,  $C_{15}H_{26}O_2$ , is an oil contained in *Spartium scoparium*, and boils at  $228^\circ$ .

### Opium Bases.

In opium, the dried juice of the green seed capsules of poppy (*Papaver somniferum*) we find not only meconic acid and meconine (p. 569) but a series of bases, of which may be mentioned:—

Morphine,  $C_{17}H_{19}NO_3$

Codeine,  $C_{18}H_{21}NO_3$

Thebaine,  $C_{19}H_{21}NO_3$

Papaverine,  $C_{21}H_{21}NO_4$

Narcotine,  $C_{22}H_{23}NO_7$

Narceine,  $C_{28}H_{29}NO_9$ .

**Morphine**,  $C_{17}H_{19}NO_3 + H_2O$ , crystallizes from alcohol in prisms, tastes bitter, and in small quantities produces sleep. It shows an alkaline reaction, and represents a tertiary, monacidic base.

The solutions of morphine and its salts are colored dark blue by ferric chloride; the solution in concentrated sulphuric acid acquires a blood-red coloration on the addition of a little nitric acid. It contains two hydroxyl groups, dissolves in potassium hydroxide, and affords alkyl and acid derivatives. It yields quinoline and phenanthrene (with phenanthrene-quinoline) and pyrrol, on distillation with zinc dust. The hydroxide obtained from ethyl morphine by addition of  $CH_3I$  and the action of silver oxide, passes into the phenanthrene derivative (*Ann.*, 222, 231) on the application of heat.

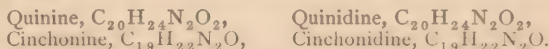
**Codeine**, **Methyl Morphine**,  $C_{17}H_{18}(CH_3)NO_3$ , is contained in opium, and is obtained from morphine by means of methyl iodide and potassium hydroxide. From ether it crystallizes in large prisms, melting at  $150^\circ$ .

**Narcotine**,  $C_{22}H_{23}NO_7$ , is separated from morphine by potassium hydroxide, in which it is insoluble. It crystallizes from alcohol in shining prisms, and melts at

176°. When boiled with water it is decomposed into meconine,  $C_{10}H_{10}O_4$  (p. 569), and cotarnine,  $C_{12}H_{13}NO_3$ . The latter crystallizes with  $1H_2O$  in prisms and is a pyridine derivative. Bromine converts it into dibrom-pyridine; when boiled with nitric acid it yields Cotarnic Acid,  $C_{11}H_{12}O_5$ , and apophyllenic acid,  $C_8H_7NO_4$  (p. 665).

### *Cinchona Bases.*

The *cinchona barks* contain, in addition to tannin and quinic acid (p. 564), a series of bases, the most important of which are:



Quinine and cinchonine are present in large quantity in so-called *Calisaya bark*, while the bases quinidine and cinchonidine, isomeric with them, predominate in other varieties of quinia barks.

**Quinine**,  $C_{20}H_{24}N_2O_2$ , is found as high as 2-3 per cent. in the yellow *Calisaya bark*. It crystallizes with  $3H_2O$  in prisms, or when anhydrous (from alcohol and ether) in silky needles, melting at 177°. It reacts alkaline, tastes bitter, and being a diacidic base forms primary and secondary salts.

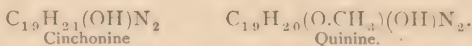
The neutral sulphate,  $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8H_2O$ , and the primary hydrochloride,  $C_{20}H_{24}N_2O_2 \cdot HCl + 2H_2O$ , are employed in medicine. The former consists of long, shining needles, which fall to a white powder on exposure. It dissolves readily in dilute sulphuric acid, the solution exhibiting a beautiful blue fluorescence.

When chlorine water and then ammonia are added to the solution of a quinine salt, there is produced a green precipitate, dissolving in an excess of ammonium hydroxide with an emerald-green color. On adding an alcoholic iodine solution to the sulphate in acetic acid, a *periodide*, called herapathite, is precipitated. This crystallizes in emerald-green plates with golden lustre, and polarizes light similar to tourmaline.

Quinine is a tertiary diamine, and with metallic iodides yields the iodides,  $C_{20}H_{24}N_2O_2 \cdot CH_3I$  and  $C_{20}H_{24}N_2O_2 \cdot 2CH_3I$ . The first of these forms (p. 669) so-called methyl quinine when it is boiled with caustic potash.

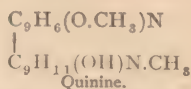
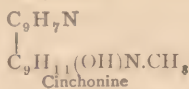
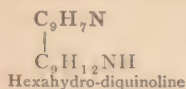
**Cinchonine**,  $C_{19}H_{22}N_2O$ , occurs principally in the gray quinia bark (*China Huanaco*) (upwards of 2.5 per cent.) It crystallizes from alcohol in white prisms, sublimes in needles in a current of hydrogen, and melts about 250°. Like quinine it seems to dissipate fever, but to a less degree.

Quinine and cinchonine contain one hydroxyl and the former an additional methoxyl group:—



They afford acetyl derivatives when heated with acetic anhydride. Quinine heated to 150° with hydrochloric acid splits off the methyl group, with formation of apoquinine,  $C_{19}H_{20}(OH)_2N_2$ , which departs itself like a bivalent phenol.

All other transformations argue in favor of the existence of a diquinoline (p. 670) as the basis of cinchonine and quinine. In it there is a hydrogenized quinoline nucleus (as in hexahydro-pyridine, p. 677) and a methyl group is attached to the nitrogen atom (*Ber.*, 14, 1582):—



Oxidation converts cinchonine into cinchoninic acid (p. 673), whereas quinine yields quininic acid (p. 674). If cinchonine be fused with alkalis it forms quinoline,  $\text{C}_9\text{H}_7\text{N}$  (together with  $\beta$ -ethyl pyridine and fatty acids), but from quinine under like treatment we get a methoxyquinoline,  $\text{C}_9\text{H}_6(\text{O}.\text{CH}_3)\text{N}$  (p. 671). These transformations destroy the hydrogenized quinoline nucleus, and its nitrogen is separated in the form of ammonia (exactly half of all the nitrogen of the quinia base (*Ann.*, 204, 90), just as hexapyridine is readily destroyed completely.

### *Bases from Strychnos.*

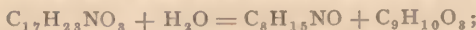
In the fruit of the different strychnos, principally in that of *Strychnos nux vomica* and in *St. Ignatius' beans* (*Strychnos Ignatii*), are found two very poisonous bases: Strychnine and brucine.

**Strychnine**,  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$ , crystallizes in four-sided prisms, melting at  $284^\circ$ , reacting alkaline and possessing an extremely bitter taste. It is a tertiary amine, and when fused with potassium hydroxide yields quinoline and indol.

**Brucine**,  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$ , crystallizes with  $4\text{H}_2\text{O}$  in prisms, and melts at  $178^\circ$  when anhydrous. It dissolves with a red color in concentrated nitric acid. On application of heat it becomes yellow and violet after the addition of stannous chloride. When distilled with potassium hydroxide it affords  $\beta$ -ethyl pyridine and two collidines.

### *Solanum Bases.*

In some varieties of *Solanum* there are found three isomeric alkaloids of very similar constitution,  $\text{C}_{17}\text{H}_{23}\text{NO}_3$ . They are atropine, hyoscyamine and hyoscyne. If they are introduced in very small quantity into the eye they cause dilatation of the pupil and are therefore employed in the treatment of the eyes. All three decompose into tropic acid (and atropic acid, p. 580), and a base,  $\text{C}_8\text{H}_{15}\text{NO}$ , when heated with hydrochloric acid or baryta water:—



by this reaction tropine is formed from atropine and hyoscyamine, but from hyoscyne we get isomeric pseudotropine. Conversely, atropine is again recovered by evaporating tropic acid and atropine with dilute hydrochloric acid.

**Atropine**, daturine,  $\text{C}_{17}\text{H}_{23}\text{NO}_3$ , is contained in the deadly nightshade (*Atropa belladonna*) and in *Datura stramonium*. It crystallizes from alcohol in small prisms, melting at  $115^\circ$ .



**Hyoscyamine**,  $C_{17}H_{23}NO_3$ , occurs in the seeds of *Hyoscyamus niger*, in *Atropa belladonna* and in *Datura stramonium*, also in *Duboisia myoporeoides*. It crystallizes from chloroform in shining needles, and melts at  $108.5^\circ$ . **Hyoscine**,  $C_{17}H_{23}NO_3$ , is a viscous liquid found in henbane.

**Belladonine**,  $C_{17}H_{23}NO_3$ , resembles these alkaloids. It occurs with atropine, and is likewise decomposed into tropic acid and tropine (*Ber.*, 17, 152, 383).

**Tropine**,  $C_8H_{15}NO$  (see above), obtained by decomposition from the preceding alkaloids, crystallizes from ether in plates, melts at  $62^\circ$ , and boils at  $229^\circ$ . It is a tertiary and powerful base. When heated with concentrated hydrochloric acid or with glacial acetic acid to  $180^\circ$ , water separates, and it yields tropidine,  $C_8H_{13}N$  (p. 679): it is, therefore, an oxy-ethyl methyl-tetrahydropyridine,  $C_5H_7(C_2H_4.OH)N.CH_3$  (*Ber.*, 15, 1031), and belongs to the so-called alkines (p. 264).

Being a tertiary amine tropine unites with methyl iodide to the body,  $C_8H_{15}NO.CH_3I$ , whose hydroxide, obtained by silver oxide, yields  $\alpha$ -**Methyltropine**,  $C_8H_{14}(CH_3)NO$ , on the application of heat. The latter affords dimethyl-tropine iodide with  $CH_3I$ , and this distilled with potassium hydroxide yields trimethylamine and **Tropilidene**,  $C_7H_8$  (boiling at  $114^\circ$ ) (*Ann.*, 217, 133) (vide *Piperylene*, p. 678).

Just as tropine yields atropine with atropic acid, so it is capable of entering combination with other acids producing ester-like derivatives, which have been called tropeïnes (Ladenburg, *Ann.*, 217, 82). Of these phenylglycolyl-tropeïne or **Homatropine**,  $C_8H_7N(CH_3).C_2H_4.O.CO.CH(OH).C_6H_5$ , is noteworthy. It is obtained from tropine and mandelic acid. It is employed as a substitute for atropine. It is very soluble in water, crystallizes in prisms, melts about  $96^\circ$ , and is applied in the form of hydrobromide.

Of the numerous other, but little studied alkaloids, we may notice:—

**Veratrine**,  $C_{22}H_{49}NO_9$ , **Cevadine**. This occurs, together with veratric acid (p. 559), and other alkaloids, in the white hellebore (from *V. album*) and in the *Sabadilla* seeds (from *V. Sabadilla*). It crystallizes from alcohol in prisms, and melts at  $205^\circ$ . It dissolves in sulphuric acid with a yellow color, which gradually changes to blood-red.

**Sinapine**,  $C_{16}H_{23}NO_5$ , occurs as sulphocyanate in white mustard. Free sinapine is very soluble, and decomposable. When boiled with alkalis it decomposes into choline (p. 265), and sinapic acid,  $C_{11}H_{12}O_5$ , which is a butylene gallic acid.

## TERPENES.

By this name are designated the hydrocarbons which are analogous to turpentine oil,  $C_{10}H_{16}$ , and occur in many of the essential oils and resins originating from the vegetable kingdom. In chemical deportment they resemble one another very closely, and are usually distinguished only by their physical properties: their boiling temperature (about  $150$ – $180^\circ$ ), their odor, and their varying deportment with reference to polarized light. All natural terpenes,

$C_{10}H_{16}$ , thus far investigated, which are optically *active*, can be, by repeated distillation, or by shaking with a little concentrated sulphuric acid, converted into one and the same *optical modification*—solid *camphene* or *terebene*,  $C_{10}H_{16}$ . The withdrawal of two hydrogen atoms from camphene and the terpenes affords us ordinary cymene,  $C_{10}H_{14}$  (normal propyl methyl-benzene). On boiling with dilute nitric acid they yield toluic and terephthalic acids (with other acids). Therefore, camphene may be assumed to be a benzene addition product—cymene dihydride,  $C_{10}H_{14} \cdot H_2$ .

There are in accord with the benzene theory, three different para-cymene dihydrides possible; yet the existence of the different optically active terpenes depends, indeed, chiefly upon isomerism relations of quite another character, just as different active tartaric acids, etc., are derived from inactive dioxysuccinic acid.

**Turpentine Oil**,  $C_{10}H_{16}$ . The resinous juice, called turpentine, exuding from various coniferæ, consists of a solution of resin in turpentine oil, which distils with steam while the resin (colophony) remains behind. The turpentines obtained from the different pines show some differences, especially in their optical rotatory powers.

The German turpentine oil (from *Pinus silvestris*), the French (from *Pinus maritima*), the Venetian (from *Larix europæa*), and others, are lævo-rotatory, while the English (from *Pinus australis*) is dextro-rotatory. Commercial oil of turpentine invariably contains acids (formic, etc.) and for its purification is shaken with sodium hydroxide and distilled in steam.

Oil of turpentine is a colorless, peculiar-smelling liquid, boiling from  $158-160^\circ$ ; its sp. gr. equals 0.86–0.89. It is almost insoluble in water, is miscible with absolute alcohol and ether, dissolves sulphur, phosphorus, resins, caoutchouc, and, therefore, serves for the preparation of oil colors and varnishes.

Oil of turpentine slowly acquires oxygen from the air (with ozone formation) and resinifies with production of acids (formic, acetic); at the same time small quantities of cymene are formed. This can also be made by shaking the turpentine with sulphuric acid ( $\frac{1}{20}$  part) and then distilling. When turpentine is boiled with dilute nitric acid, different fatty acids, terebinic acid, toluic acid and terephthalic acid result. Chromic acid converts it into terpenylic acid,  $C_8H_{12}O_4$  (p. 365); terephthalic acid then seems to form only if cymene be present in the oil of turpentine.

Chlorine unites with oil of turpentine at  $-15^\circ$ , forming a viscous **Dichloride**,  $C_{10}H_{16}Cl_2$ , which splits into  $2HCl$  and cymene when heat is applied to it. When the **Dibromide**,  $C_{10}H_{16}Br_2$ , is digested with feeble bases (aniline) it affords cymene, which is also produced on boiling turpentine oil with iodine.

The hydrides of oil of turpentine are: **Hydrocamphene**,  $C_{10}H_{18}$ , which is produced, along with camphene, from borneol chloride,  $C_{10}H_{17}Cl$ , when sodium acts upon it. It is a white mass, melting at  $140^\circ$  and subliming readily. **Menthene**,  $C_{10}H_{18}$ , from menthacamphene,  $C_{10}H_{20}O$ , by  $P_2O_5$ , is a liquid, and boils at  $167^\circ$ . **Terpene tetrahydride**,  $C_{10}H_{20}$ , formed from oil of turpentine on heating it with phosphonium iodide, boils at  $160^\circ$ .

If oil of turpentine containing water be permitted to stand for some time, or if acted upon by sulphuric acid or hydrochloric acid (*Ber.*, 12, 1406) it yields

**terpine hydrate**,  $C_{10}H_{16} \cdot 2H_2O + H_2O$ . This consists of large rhombic crystals, without odor, and easily soluble in hot water, alcohol and ether. It melts near  $100^\circ$ , loses water, and passes into the so-called anhydrous **terpine**,  $C_{10}H_{16} \cdot 2H_2O$ , melting at  $103^\circ$ , and subliming in fine needles. If the aqueous solution of terpene be heated with a little hydrochloric acid, or if terpene dihydrochloride,  $C_{10}H_{16} \cdot 2HCl$ , be boiled with water or alcoholic potash we obtain **terpinol**,  $(C_{10}H_{16})_2 \cdot H_2O$ , an oil with an odor resembling that of hyacinths, and boiling at  $168^\circ$ .

With hydrogen chloride turpentine forms  $C_{10}H_{16} \cdot HCl$  and  $C_{10}H_{16} \cdot 2HCl$ . **Terpene Mono-hydrochloride**,  $C_{10}H_{16} \cdot HCl$ , is produced on conducting  $HCl$  gas into oil of turpentine; the solution generates heat, and on cooling a crystalline compound separates. The hydrochloride (called *artificial camphor*) yields crystals resembling those of camphor, has the odor of the latter, melts at  $125^\circ$ , boils at  $210^\circ$ , and sublimes in needles. The hydrochloride from the French and American oil of turpentine is lævo-rotatory, that from the English dextro-rotatory, and melts at  $131^\circ$ .

**Terpene Dihydrochloride**,  $C_{10}H_{16} \cdot 2HCl$ , is obtained on leading  $HCl$  into the alcoholic solution of oil of turpentine, avoiding an increase of temperature. Water separates it as an oil which solidifies to a crystalline mass. The same dihydrochloride is obtained from all the different oils of turpentine; it crystallizes in plates, and melts at  $49^\circ$ .

The *Camphenes* are the solid terpenes,  $C_{10}H_{16}$ , mostly obtained from the hydrochlorides of the terpenes on heating them with alcoholic potash or with fatty acid salts. The camphenes derived from the various oils of turpentine show some points of difference, chiefly in their rotatory power. They melt at  $45-52^\circ$ , and all boil about  $160^\circ$ .

With  $HCl$  they yield solid hydrochlorides, from which alcoholic potash regenerates the camphenes. Chromic acid oxidizes them to camphor (active and inactive).

**Terecamphene**, from French oil of turpentine, is lævo-rotatory, and melts at  $45-48^\circ$ . **Austracamphene**, from the English oil of turpentine, is very similar to the preceding, but is dextro-rotatory. **Borneocamphene** (camphor camphene), from Borneol-chloride,  $C_{10}H_{17}Cl$  (from borneol and  $HCl$ ) on heating with alcoholic potash, and from camphor chloride,  $C_{10}H_{16}Cl_2$  (p. 685), by action of sodium, melts at  $51-52^\circ$ , and when molten is dextro-rotatory.

**Inactive Camphene** (Terebene), formed on shaking the turpentine oil repeatedly with sulphuric acid (together with cymene, terpilene, etc.) (p. 683), affords crystals resembling ammonium chloride, melts at  $50^\circ$ , and boils at  $160^\circ$ .

**Other liquid terpenes**,  $C_{10}H_{16}$ , are:—

**Isoterpene**, obtained by heating terpene hydrate with acetic anhydride. It boils at  $179^\circ$ . **Terpilene**, produced along with terebene (see above), boils at  $178^\circ$ . **Borneène**, obtained from borneo-camphene with  $P_2O_5$ , boils at  $178^\circ$ .

The following have been isolated from essential oils:—

**Citrene**, from lemon oil, boils at  $173^\circ$ ; **Hesperidene**, from orange oil (at  $176^\circ$ ); **Thymene**, (together with cymene and thymol), from oil of thyme, (at  $160-165^\circ$ ); **Carvene** (with carvol,  $C_{10}H_{14}O$ ), from Caraway oil, at  $176^\circ$ ; **Olibene**, from oil of frankincense, at  $157^\circ$ , and **Eucalyptene**, from Australian Eucalyptus oil, etc.

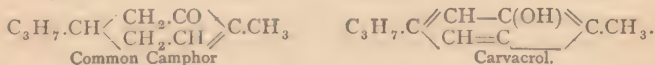
*Homologous terpenes* have been obtained by letting sodium act upon a mixture of camphor dichloride,  $C_{10}H_{16}Cl_2$  (melting at  $155^\circ$ ) (p. 685), and alkyl iodides.

**Ethyl Camphene**,  $C_{10}H_{15}(C_2H_5)$ , is a liquid with an odor resembling that of oil of turpentine, and boiling at  $198-200^\circ$ . **Isobutyl Camphene**,  $C_{10}H_{15}(C_4H_9)$ , boils at  $228^\circ$ .

**Polymeric Terpenes**,  $C_{15}H_{24}$ , boiling at  $250-270^\circ$ , have been separated from oil of juniper-berries, from Cubeba oil and Copaiva oil. **Colophene** is a *diterpene*,  $C_{20}H_{32}$ , obtained by distilling colophony and by the action of sulphuric acid upon turpentine oil. It boils at  $318^\circ$ .

## CAMPHOR.

The camphors are peculiar-smelling substances, containing oxygen and intimately related to the terpenes. They are often found with the latter in plant secretions, and can be artificially prepared (in slight quantities) by oxidizing the same. Japan camphor,  $C_{10}H_{16}O$ , bears the same relation to Borneo camphor,  $C_{10}H_{18}O$ , as a ketone to a secondary alcohol. In accord with this, it yields an acetoxim with hydroxylamine. Distilled with  $ZnCl_2$  or  $P_2O_5$ , ordinary camphor furnishes cymene (p. 419); heated with iodine it forms oxycymene (Carvacrol, p. 495). Hence its constitution (according to A. Kekulé) can be expressed by the following formula (Comp., *Ber.*, 16, 2260):—



Common or Japan camphor is found in the camphor-tree (*Laurus Camphora*) indigenous to Japan and China. It is obtained by distillation with steam and sublimation. It is prepared artificially (in small amounts) by oxidizing terpenes and camphenes. It is a colorless, transparent mass, and crystallizes from alcohol, or by sublimation, in shining prisms, of sp. gr. 0.985. It volatilizes already at ordinary temperatures, melts at  $175^\circ$ , and distils at  $204^\circ$ . Its alcoholic solution is dextro-rotatory. Camphor yields pure cymene (p. 419), if distilled with  $P_2O_5$ , and on boiling with iodine affords carvacrol (p. 495). When boiled with nitric acid it yields different acids, chiefly camphoronic acids. The Camphoroxim,  $C_{10}H_{16}(N.OH)$ , obtained with hydroxylamine, melts at  $115^\circ$  (*Ber.*, 17, 805).

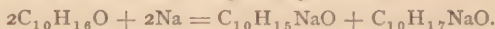
Chlorine led into the alcoholic solution of camphor produces two **mono-chlor-camphors**,  $C_{10}H_{15}ClO$ , melting at  $84^\circ$  and  $100^\circ$  respectively. The latter modification can be changed into the first. There are also two **Dichlorcamphors**,  $C_{10}H_{14}Cl_2O$  (*Ber.*, 16, 218).  $PCl_5$  converts camphor into two **Camphor-dichlorides**,  $C_{10}H_{16}Cl_2$ , melting at  $70^\circ$  and  $75^\circ$ .

Bromine produces **Monobrom-camphor**,  $C_{10}H_{15}Br$ , melting at  $84^\circ$ , and two **Dibromcamphors**,  $C_{10}H_{14}Br_2O$ , melting at  $61^\circ$  and  $115^\circ$ ; the first modification changes to the second when heated with bromine.

On warming brom-camphor with nitric acid we obtain **nitrocamphor**,  $C_{10}H_{15}(NO_2).O$ , melting at  $83^\circ$ .  $HgNa$  reduces it to **amido-camphor**,  $C_{10}H_{15}(NH_2)O$  (a wax-like mass, boiling at  $246^\circ$ ).



On allowing sodium to act on camphor dissolved in toluene, a mixture of **sodium camphor** and **Borneol camphor** separates:—



The alkyl iodides convert these sodium derivatives into alkyl compounds. **Ethyl Camphor**,  $\text{C}_{10}\text{H}_{15}(\text{C}_2\text{H}_5)\text{O}$ , is a liquid, boiling at  $230^\circ$ .

**Carvol**,  $\text{C}_{10}\text{H}_{14}\text{O}$  (p. 495), is closely related to common camphor, and like the latter contains a ketone group, inasmuch as it unites with hydroxylamine and phenyl hydrazine (*Ber.*, 17, 1577).

The camphors, like the turpentine oils, occurring in different plants, manifest some differences. **Matricaria camphor** contained in the oil of *Matricaria Parthenium* is lævo-rotatory, and when oxidized with nitric acid yields lævo-camphoric acid. **Absinthol**, from oil of wormwood (from *Artemisia Absinthium*), is liquid, and boils at  $195^\circ$ . Similar liquid camphors have also been obtained by oxidizing some terpenes. **Caryophyllin**,  $\text{C}_{20}\text{H}_{32}\text{O}$ , is a polymeric camphor, contained in cloves, and melts above  $300^\circ$ .

**Borneol, Borneo Camphor**,  $\text{C}_{10}\text{H}_{18}\text{O} = \text{C}_{10}\text{H}_{17}\text{OH}$ , occurs in *Dryobalanops Camphora*, a tree growing in Borneo and Sumatra. It is artificially prepared by acting with sodium upon the alcoholic solution of common camphor (*Ber.*, 17, 1037). It is quite like Japan camphor, and has a peculiar odor resembling that of pepper-mint. It sublimes in six-sided leaflets, melts at  $198^\circ$ , and boils at  $212^\circ$ . Its alcoholic solution is dextro-rotatory.

Nitric acid oxidizes borneol first to common camphor, and then to camphoric and camphoronic acids. As an alcohol it unites, on application of heat, with organic acids or acid anhydrides, forming esters; these are partly solid and partly liquid. The acetyl ester,  $\text{C}_{10}\text{H}_{17}\text{O} \cdot \text{C}_2\text{H}_3\text{O}$ , boiling at  $221^\circ$ , is also obtained from camphene hydrochloride,  $\text{C}_{10}\text{H}_{16}\text{HCl}$  (from camphor camphene, p. 684), with silver acetate. When borneol is heated with  $\text{P}_2\text{O}_5$ , it yields **Borneone**,  $\text{C}_{10}\text{H}_{16}$ . **Borneol Chloride**,  $\text{C}_{10}\text{H}_{17}\text{Cl}$ , melting at  $148^\circ$ , is produced by means of  $\text{PCl}_5$  or concentrated hydrochloric acid.

**Menthol, Mentha Camphor**,  $\text{C}_{10}\text{H}_{20}\text{O}$ , separates in crystalline form, on cooling, from peppermint oil (from *Mentha piperita*). It melts at  $42^\circ$ , boils at  $213^\circ$ , and is lævo-rotatory. It affords *esters* with acids and with concentrated hydrochloric acid it yields liquid *menthol chloride*,  $\text{C}_{10}\text{H}_{19}\text{Cl}$ . If distilled with  $\text{P}_2\text{O}_5$  it forms *Menthene*,  $\text{C}_{10}\text{H}_{18}$  (p. 683).

The oxidation of the camphors affords different acids, whose constitution has not yet been explained.

**Campholic Acid**,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , is produced on distilling camphor over heated soda-lime. It melts at  $95^\circ$ , and is oxidized by nitric acid to camphoric and camphoronic acids.

**Camphoric Acid**,  $\text{C}_{10}\text{H}_{16}\text{O}_4 = \text{C}_8\text{H}_{14}(\text{CO}_2\text{H})_2$ , is obtained by boiling camphor with nitric acid (*Ann.*, 163, 323), when three oxygen atoms are directly fixed. It crystallizes from hot water in colorless leaflets, melts at  $178^\circ$ , and decomposes into water and its anhydride,  $\text{C}_8\text{H}_{14}(\text{CO})_2\text{O}$ ; the latter sublimes readily in shining needles, melts at  $217^\circ$ , and boils at  $270^\circ$ .

The acid from common camphor is dextro-rotatory, that from *Matricaria* camphor is, however, lævo-rotatory. The inactive paracamphoric acid is produced on mixing the two acids.

By the fusion of camphoric acid with potash we get isopropyl succinic acid (p. 332) and, therefore, it is very probable that its constitution is represented by the formula,  $C_3H_7 \cdot CH \begin{matrix} < CH: C(CH_3)CO_2H \\ < CH_2 \cdot CO_2H \end{matrix}$  (*Ann.*, 220, 278).

**Camphoronic Acid**,  $C_9H_{12}O_5$ , produced in the preparation of camphoric acid, crystallizes with  $1H_2O$ , melts at  $115^\circ$  when anhydrous, and distils undecomposed.

## RESINS.

The resins are closely related to the terpenes, and occur with them in plants, and are also produced by their oxidation in the air. Their natural, thick solutions in the essential oils and turpentine are called *balsams*, whereas the real *gum resins* are amorphous, mostly vitreous bodies. Their solutions in alcohol, ether or turpentine oils constitute the commercial varnishes.

Most natural resins appear to consist of a mixture of different, peculiar acids, the resin acids. The alkalis dissolve them, forming *resin soaps*, from which acids again precipitate the *resin acids*. By their fusion with alkalis we obtain different benzene derivatives (resorcinol, phloroglucin, proto-catechuic acid); and when they are distilled with zinc dust they yield benzenes, naphthalenes, etc.

*Colophony* is found in turpentine (p. 683), and, in the distillation of the latter, remains as a fused mass. It consists principally of **Abietic Acid**,  $C_{44}H_{64}O_5$  (Sylvic acid), which can be extracted by hot alcohol, crystallizes in leaflets, and melts at  $139^\circ$  ( $165^\circ$ ). When oxidized it yields trimellitic, isophthalic and terebinic acids.

*Gallipot Resin*, from *Pinus maritima*, contains **pimaric acid**,  $C_{20}H_{30}O_2$ , which is very similar to sylvic acid and passes into the latter when distilled in vacuo.

*Gum lac*, obtained from East India fig trees, constitutes what is known as shellac when fused. This is employed in the preparation of sealing wax and varnishes.

*Amber* is a fossil resin, found in peat-bogs. It consists of succinic acid, two resin acids and a volatile oil. After fusion it dissolves easily in alcohol and turpentine oil, and serves for the preparation of varnishes.

To the *gum resins*, occurring mixed with vegetable gums, and gum in the juice of plants, belong gamboge, euphorbium, asafoetida, caoutchouc and gutta serena.

## GLUCOSIDES.

These substances occur in plants and split into sugars (mostly grape sugar), and other bodies (alcohols, aldehydes, phenols), when acted on by acids or ferments. Therefore they are assumed to be ethereal derivatives of the glucoses. Various members of this series, obtainable also by synthesis, have already received notice in con-

nection with the products they yield when they are decomposed. Of those less understood are:—

**Æsculin**,  $C_{15}H_{16}O_9$ , contained in the bark of the horse chestnut; it crystallizes in fine needles with  $1\frac{1}{2}$  molecules  $H_2O$ , melts when anhydrous at  $160^\circ$ , and is decomposed by acids or ferments into glucoses and æsculetin,  $C_9H_6O_4$  (Dioxy-coumarin, p. 588). **Daphnin**,  $C_{15}H_{16}O_9 + H_2O$ , is isomeric with æsculin, and is obtained from the bark of *Daphne alpina*. It melts at  $200^\circ$ , and breaks up into glucose and daphnetin (Dioxycoumarin, p. 588).

**Arbutin**,  $C_{12}H_{16}O_7$ , and **Methyl Arbutin**,  $C_{13}H_{18}O_7$ , are found in the leaves of *Arbutus uva ursi*. By their decomposition we get, besides grape sugar, hydroquinone or methyl hydroquinone. Arbutin crystallizes in fine needles, with  $\frac{1}{2}$ -1 molecule water, melts at  $187^\circ$  (*Ber.*, 16, 1925) in the anhydrous state, and is colored a deep blue by ferric chloride. Methyl arbutin contains  $1H_2O$ , and melts at  $176^\circ$ . It is formed artificially from arbutin by the action of methyl iodide and potash, and from methyl hydroquinone with aceto-chlorhydrose (p. 385).

**Hesperidin**,  $C_{22}H_{26}O_{12}$ , is present in the unripe fruit of oranges, lemons, etc. It separates from alcohol in fine needles, melts at  $251^\circ$ , and is decomposed into grape sugar and **Hesperitin**,  $C_{16}H_{14}O_6$ , which by further boiling with KOH breaks up into hesperitinic acid (isoferulic acid, p. 586), and phloroglucin,  $C_6H_3(OH)_3$ .

**Phloridzin**,  $C_{21}H_{24}O_{10}$ , occurs in the root bark of various fruit-trees, crystallizes with  $2H_2O$  in fine prisms, and when anhydrous melts at  $108^\circ$ . By decomposition it yields grape sugar and **Phloretin**,  $C_{15}H_{14}O_{15}$  (colorless leaflets), which alkalis convert into phloretic acid (p. 555), and phloroglucin.

**Quercitrin**,  $C_{36}H_{38}O_{20}$ , is found in the bark of *Quercus tinctoria*, and is applied as a yellow dye under the name *Quercitrone*. It consists of yellow needles or leaflets, which are decomposed into isodulcitol (p. 378), and **Quercetin**,  $C_{24}H_{16}O_{11} + 3H_2O$ . The latter forms an *hexa-ethyl* and *octo-acetyl* derivative (*Ber.*, 17, 1680). Fused with alkalis it affords protocatechuic and other acids.

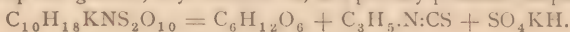
**Saponin**,  $C_{32}H_{54}O_{18}$ , in the roots of *Saponaria officinalis*, is a white amorphous powder, provoking sneezing, and in aqueous solution forms a strong lather. Its decomposition products are glucose and sapogenin,  $C_{14}H_{22}O_4$ .

Glucosides whose decomposition products belong to the fatty-series are:—

**Convolvulin**,  $C_{31}H_{50}O_{16}$ , derived from the roots of Jalap (from *Convolvulus purga*). It is a gummy mass, and is a strong purgative. It dissolves in alkalis to **Convolvulic Acid**,  $C_{31}H_{52}O_{17}$  (?), which nitric acid converts into **Ipomic Acid**,  $C_{10}H_{18}O_4 = C_8H_{16}(CO_2H)_2$ .

**Jalapin**,  $C_{34}H_{56}O_{16}$ , from *Convolvulus orizabensis*, is very similar to convolvulin, and affords analogous derivatives.

**Myronic Acid**,  $C_{10}H_{19}NS_2O_{10}$ , occurs as potassium salt in the seeds of black mustard. This crystallizes from water in bright needles. On boiling it with baryta water, or by the action of the ferment *myrosin*, present in the seed, the salt splits up into glucose, allyl mustard oil, and primary potassium sulphate:—



## BITTER PRINCIPLES.

Under the head of "bitter principles" or indifferent substances is embraced a class of vegetable bodies whose chemical character is but indistinctly indicated. Many of them have already found their place in the chemical system. Those as yet uninvestigated are:—

**Aloin**,  $C_{17}H_{18}O_7$ , found in aloes, the dried sap of many plants of the aloe variety. It forms fine needles, possesses a very bitter taste, and acts as a strong purgative. If digested with nitric acid it yields *aloetic acid*,  $C_{14}H_4(NO_2)_4O_2$ , and *chrysammic acid* (p. 642).

**Cantharidin**,  $C_{10}H_{12}O_4$ , contained in Spanish flies and other insects, crystallizes in prisms or leaflets, melts at  $218^\circ$ , and sublimes readily. It tastes very bitter and produces blisters on the skin.

**Picrotoxin**,  $C_{30}H_{34}O_{13}$ , appears to be a mixture of *picrotoxinin* and *picrotin*, into which it readily resolves itself (*Ber.*, 17, Ref. 210). It is found in the grains of cockle, and crystallizes in fine needles.

**Santonin**,  $C_{15}H_{18}O_3$ , is the active principle of worm-seed, crystallizes in shining prisms, and melts at  $170^\circ$ . It dissolves in alkalies to salts of **Santonic Acid**,  $C_{15}H_{20}O_4$ , from which acids reprecipitate the santonin. On boiling with baryta water we have formed salts of isomeric *santoic acid*,  $C_{15}H_{20}O_4$ , which melts at  $160-163^\circ$ . Santonin, therefore, bears the same relation to these two acids as coumarin to coumarinic and coumaric acids. When santonin is boiled with hydriodic acid and phosphorus we get two isomeric acids,  $C_{15}H_{20}O_3$  (santoic acids), which on heating with baryta water afford a dimethyl naphthol,  $C_{10}H_5(CH_3)_2.OH$  (*Ber.*, 16, 827).

The following are some of the unstudied coloring matters; some of them appear to have a constitution analogous to the phthaleïns (p. 627):—

**Brasilin**,  $C_{16}H_{14}O_5$ , is found in Brazil-wood and red wood; crystallizes in white, shining needles, and dissolves in alkalies with a carmine-red color. When distilled it yields *resorcinol*.

**Carthamin**,  $C_{14}H_{16}N_7$ , occurs in safflower, the blossoms of *Carthamus tinctorium*, and is precipitated from its soda solution by acetic acid, as a dark red powder, which, on drying, acquires a metallic lustre. It dissolves with a beautiful red color in alcohol and the alkalies. It yields *para-oxybenzoic acid* with KOH.

**Curcumin**,  $C_{14}H_{14}O_4$ , the coloring matter of turmeric, crystallizes in orange-yellow prisms, melts at  $177^\circ$ , and dissolves in the alkalies to brownish-red salts. Ethyl vanillic acid is obtained on oxidizing diethyl-curcumin with  $MnO_4K$ .

**Euxanthin**,  $C_{19}H_{16}O_{10}$ , occurs as magnesia salt in so-called *purée* (*jaune indien*), a yellow coloring matter from India and China, of unknown origin. It crystallizes from alcohol in yellow prisms. When boiled with dilute sulphuric acid it splits up into glycuronic acid and **euxanthon**,  $C_{13}H_8O_4$ , which sublimes in yellow needles, and melts at  $232^\circ$ . If fused with KOH it yields *euxanthonic acid*,  $C_{13}H_{10}O_3$ , and then *hydroquinone*. When distilled with zinc dust it affords so-called *methylene diphenyl oxide*,  $C_{13}H_{10}O$  (p. 611).

**Hæmatoxylin**,  $C_{16}H_{14}O_6$ , the coloring matter of logwood (*Hæmatoxylon Campechianum*), is very soluble in water and alcohol, and crystallizes in yellowish prisms with  $3H_2O$ . It dissolves in alkalies with a blue color. When distilled or fused with KOH *pyrogallic acid* and *resorcinol* result from it. If the ammonium hydroxide solution be allowed to stand exposed to the air there results **hæmatein-ammonia**,  $C_{16}H_{11}(NH_4)O_6$ , from which acetic acid liberates **Hæmatein**,  $C_{16}H_{12}O_6$ , a red-brown powder with metallic lustre, when dried.

**Gentisin**,  $C_{14}H_{16}O_5$ , contained in the Gentian root, crystallizes in yellow needles, and fused with KOH yields *hydroquinone carboxylic acid* (p. 558) and *phloroglucin*.

**Carminic Acid**,  $C_{17}H_{18}O_{10}$ , occurs in the buds of some plants, and especially in *cochineal*, an insect inhabiting different varieties of cactus. It is an



amorphous purple-red mass, very readily soluble in water and alcohol, and yields red salts with the alkalis. When boiled with dilute sulphuric acid it splits into a non-fermentable sugar and **carmine-red**,  $C_{11}H_{12}O_7$ . When distilled with zinc dust it affords the hydrocarbon,  $C_{16}H_{12}$ . On boiling carminic acid with nitric acid we get **Trinitrocresotinic acid**,  $C_8H_5(NO_2)_3O_3 + H_2O$ , called **nitrococcic acid**.

**Chlorophyll** occurs in the chlorophyll granules in all the green parts of plants. Wax and other substances are associated with it. We do not yet know its constitution. There seems to be an essential quantity of iron in it.

The following are some *animal substances* the more extended discussion of which belongs to the province of physiological chemistry.

### BILIARY SUBSTANCES.

In the bile, the liquid secretion of the liver, essential to the digestion of fats, occur (in addition to fats, mucous substances and albuminoids) the sodium salts of two peculiar acids, glycocholic and taurocholic; also cholesterine and bile pigments (bilirubin, biliverdin).

**Cholesterine**,  $C_{26}H_{44}O$  (or  $C_{25}H_{42}O$ ), occurs in not only the bile, but in the blood, in the brain, and in the yolk of eggs, also in the seed and sprouts of many plants, in which it is often confounded with the fats. It is soluble in alcohol and ether, crystallizes in mother-of-pearl leaflets, containing  $1H_2O$ , and possessing a fatty feel. It parts with its water of crystallization at  $100^\circ$ , melts at  $145^\circ$ , and distils at  $360^\circ$  with scarcely any decomposition. If sulphuric acid be added to the chloroform solution of cholesterine, the chloroform acquires a purple-red color, and on evaporation assumes a blue, then green, and finally a violet coloration. Chemically cholesterine behaves like a monovalent alcohol, and affords esters with acids.

**Glycocholic Acid**,  $C_{26}H_{43}NO_6$ , is separated in crystalline form from its sodium salt (see above) by dilute sulphuric acid, is difficultly soluble in water, and affords crystalline salts with one equivalent of base. On adding a sugar solution and concentrated sulphuric acid to glycocholic acid we obtain a purple-red color. Boiled with alkalis it decomposes into glycocoll and **cholic acid** (cholalic acid),  $C_{24}H_{41}O_5$ , crystallizing from alcohol and ether with  $2\frac{1}{2}H_2O$  in brilliant quadratic octahedra, which effloresce in the air. It is a monobasic acid; its esters are crystalline.

**Taurocholic Acid**,  $C_{26}H_{45}NSO_7$ , is very soluble in water and alcohol, crystallizes in fine needles, and when boiled with water breaks up into cholic acid and taurine (p. 267).

For the separation of glycocholic acid and taurocholic acid from bile see *Journ. pract. Chem.*, 19, 305.

### GELATINOUS TISSUES AND GELATINES.

These are mostly nitrogenous, organized substances, which on boiling with water are converted into gelatines and are distinguished as *collagenes* and *chondrogenes*. The former constitute bone cartilage and sinews, the connective tissues, the skin and fish-bladder, and afford the ordinary true gelatine; the latter, contained in the un-

hardened cartilage, yield chondrin. As regards composition, both are very similar to the albuminoids, but differ from the latter, mainly in that they are not precipitated by nitric acid and potassium ferrocyanide.

**Glutin** is precipitated from its aqueous solution by alcohol, and when pure is a colorless, solid mass, without odor and taste. In cold water it swells up, and on boiling dissolves to a thin solution, which gelatinizes on cooling. By the addition of concentrated acetic acid or protracted boiling with a little nitric acid, the solution loses the property of gelatinizing (liquid gelatine). Tannic acid precipitates from the aqueous solution gelatine tannate, a yellowish, glutinous precipitate. The substances yielding gelatine combine also with tannic acid, withdrawing the latter completely from its solutions and forming leather.

Glycocoll and leucine are the principal substances produced on boiling gelatine with sulphuric acid or alkalis. Dry distillation produces bases of the fatty and pyridine series (p. 401).

**Chondrin**, from bone cartilage, is very similar to the preceding, and is distinguished from it by the fact that it is precipitated from its aqueous solution by alum, lead acetate, and most metallic salts; on the other hand, it is not precipitated by mercuric chloride, whereas it is otherwise with glutin. It affords leucine and not glycocoll if boiled with dilute sulphuric acid.

## ALBUMINOID SUBSTANCES, ALBUMINATES.

These were formerly known as protein substances, and form the principal constituent of the animal organism. They also occur in plants (chiefly in the seeds), in which they are produced exclusively. When absorbed into the animal organism as nutritive matter they sustain but very slight alteration in the process of assimilation.

They exhibit great conformity in their properties and especially in their composition, as seen from the following percentage numbers of the three most important varieties of albumen:—

	Albumen.	Fibrin.	Casein.
C	53.5 per cent.	52.7 per cent.	53.8 per cent.
H	7.0 " "	6.9 " "	7.2 " "
N	15.5 " "	15.4 " "	15.6 " "
O	22.4 " "	23.8 " "	22.5 " "
S	1.6 " "	1.2 " "	0.9 " "

Owing to indistinct chemical character and great power of reaction, no accurate molecular formulas could be deduced for the albuminoids up to the present. The formula of Lieberkühn,  $C_{72}H_{112}SN_{18}O_{22}$ , affords an approximate representation.

The decomposition products of the albuminoids give us an idea as to their constitution. These they afford when boiled with dilute sulphuric or hydrochloric acid, or with baryta water.

The decomposition products are mainly amido-acids of the fatty series: glycocoll, leucine, aspartic and glutamic acids, as well as

phenylamidopropionic acid, tyrosine, etc. All albuminoids yield the same products, only in relatively different amounts, therefore they must be assumed to form from the union of these constituents. Putrefaction causes a similar decomposition, but in addition to amido-acids, fatty acids and aromatic acids, as well as phenols, indol and skatole are also formed.

Most albuminoids exist in two modifications, one *soluble*, the other *insoluble* in water. Alcohol, ether, tannic acid, many mineral acids and metallic salts reprecipitate them from their aqueous solution. In their coagulated condition they are dried, white, amorphous masses. Most of them dissolve in dilute mineral acids, all, however, in concentrated acetic acid and in phosphoric acid on application of heat. Ferro- and ferri-cyanide of potassium precipitate them from their dilute acetic acid solution. They dissolve in dilute alkalies separating sulphur in form of sulphide. The substances reprecipitated by dilute acetic acid are very similar to the albuminoids employed.

*Reactions.*—All albuminoids are colored a violet red on warming with a mercuric nitrate solution containing a little nitrous acid (this is like tyrosine). On the addition of sugar and concentrated sulphuric acid they acquire a red coloration, which on exposure to the air becomes a dark violet. If concentrated sulphuric acid be added to the acetic acid solution of albuminoids they receive a violet coloration and show a characteristic absorption band in the spectrum.

Gastric juice, pepsine, dilute hydrochloric acid and various other ferments dissolve the albuminoids at  $30-40^{\circ}$ , converting them into so-called *peptones*, which dissolve readily in water, are not coagulated by heat and not precipitated by most of the reagents (*Ber.*, **16**, **1152**).

The manner of distinguishing and classifying the various albuminoids is as yet very uncertain. According to the manner in which they pass from the soluble into the insoluble state we distinguish three principal groups of albuminoids: the *albumins*, *fibrins* and *caseins*. The first are soluble in pure water, coagulate when heated alone or after acidulation with a few drops of nitric acid, and are then no longer soluble in dilute potassium hydroxide or acetic acid. The fibrins coagulate immediately after their exit from the animal organism. The caseins (legumins) are almost insoluble in water, dissolve, however, very readily in dilute alkalies and alkaline phosphates, and are again precipitated from these solutions on acidulating them.

The albumins exist in the following varieties:—

*Egg Albumin* is obtained by precipitating the aqueous solution with basic lead acetate, decomposing the precipitate with  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , and then reducing the filtrate at a temperature below  $60^{\circ}$ . It is a yellowish, gummy mass, which swells up in water and then dissolves. The perfectly neutral solution coagulates at  $72-73^{\circ}$ ; it is levo-rotatory and is precipitated by alcohol, by shaking with ether and by dilute acids.

*Serum Albumin* occurs in the blood, in the lymph and in the various secretions. It is obtained from the blood serum diluted with water (subsequent to the removal of other albuminoids by a little acetic acid) in the same manner as egg albumin. It resembles the latter, but is not precipitated by dilute mineral acids.

*Vegetable albumin* occurs in almost all vegetable juices. It coagulates on warming and is very similar to egg fibrin. *Vitellin*, contained dissolved in the yellow of the egg, appears to be a mixture of albumin and casein.

#### *Fibrins.*

*Blood fibrin* separates from the blood after the latter has been discharged from the organism. It seems to be not already formed in the blood, but to result by the union of the so-called *fibrinoplastic* (contained in the serum) and *fibrinogen* (in the blood corpuscles) *substances*. Fibrin is obtained by whipping the fresh blood, when it separates in long fibres, which are freed of blood corpuscles by long-continued kneading under water. It is a whitish, sticky, fibrinous mass, which becomes hard and brittle upon drying. It is insoluble in water, dilute hydrochloric acid and a solution of common salt.

*Myosin* constitutes (with water) the chief constituent of the muscles, in which it seems to exist in a dissolved state. It is obtained by dissolving the well washed muscles in moderately dilute sodium chloride solution and precipitating the filtrate with salt. *Vegetable fibrin* occurs in an undissolved state in the grain granules. On kneading flour (stirred to a paste) under water, the starch granules are washed out, together with the soluble albumin; and there remains a pasty mass called gluten, which, according to Ritthausen, consists of *glicidin* (vegetable gelatine), *mucedin* and *gluten fibrin*. The latter is insoluble in dilute alcohol and acids. When seeds sprout the vegetable fibrin is converted into the soluble ferment called *diastase*. The other unformed ferments (p. 382) appear also to be modified albuminoids.

#### *Caseins.*

*Milk casein* occurs dissolved in the milk of all mammalia, and on the addition of some hydrochloric acid separates as a flocculent precipitate, which is washed out with water, alcohol and ether (for the removal of the fats). Pure casein is not soluble in water, but in such containing a little hydrochloric acid or alkali. When the solutions are neutralized it is reprecipitated. The solutions do not coagulate until heated to 130–140°. If a few drops of hydrochloric acid or rennet be added to milk all the casein will be coprecipitated with the fat globules (cheese); in the solution (whey) remain milk sugar, lactic acid and salts.

*Vegetable Casein* or Legumin, occurs chiefly in the seeds of leguminous plants, and is perfectly similar to casein. It is precipitated from the pressed out juice by acids or rennet.

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In concluding the albuminates we will yet call attention to *hæmoglobin* and *lecithin*.

The *oxyhæmoglobins* are found in the arterial blood of animals and may be obtained in crystalline form from the blood corpuscles by treatment with a solution of sodium chloride and ether and the addition of alcohol. The different oxyhæmoglobins, isolated from the blood of various animals, exhibit some variations, especially in crystalline form. They are bright red, crystalline powders, very soluble in cold water, and are precipitated in crystalline form by alcohol. When the aqueous solution of oxyhæmoglobin is put under the air pump or through the agency of reducing agents (ammonium sulphide) it parts with oxygen and becomes *hæmoglobin*. The latter is also present in venous blood and may be separated out in a crystalline form. Its aqueous solution absorbs oxygen very rapidly from the air, and reverts again to oxyhæmoglobin. Both bodies in aqueous solution exhibit characteristic absorption spectra, whereby they may be easily distinguished.

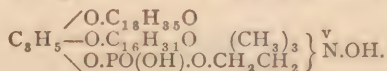


If carbon monoxide be conducted into the oxy-hæmoglobin solution, oxygen is also displaced and hæmoglobin-carbon monoxide formed. This can be obtained in large crystals with a bluish color. This explains the poisonous action of carbon monoxide. The bluish, red solution of hæmoglobin-carbon monoxide shows two characteristic absorption spectra. These do not disappear upon the addition of ammonium sulphide (distinction from oxy-hæmoglobin).

On heating to  $70^{\circ}$ , or through the action of acids or alkalis, oxyhæmoglobin is split up into albuminoids, fatty acids and the pigment *hæmatin*, which in a dry condition is a dark brown powder. It contains 9 per cent. iron, and, as it appears, corresponds to the formula,  $C_{34}H_{34}FeN_4O_5$ .

The addition of a drop of glacial acetic acid and very little salt to oxyhæmoglobin (or dried blood) aided by heat, produces microscopic reddish-brown crystals of hæmin (hæmin hydrochloride); alkalis separate hæmatin again from it. The production of these crystals serves as a delicate reaction for the detection of blood.

*Lecithin*,  $C_{42}H_{86}NPO_9$  (Protagon), is widely distributed in the animal organism and occurs especially in the brain, in the nerves, the blood corpuscles and the yellow of egg, from which it is most easily prepared. It is a wax-like mass, easily soluble in alcohol and ether, and crystallizes in fine needles. It swells up in water and forms an opalescent solution, from which it is reprecipitated by various salts. It unites with bases and acids to salts, forming a difficultly soluble double salt  $(C_{42}H_{84}NPO_8 \cdot HCl)_2 \cdot PtCl_4$ , with platinic chloride. Lecithin decomposes into choline, glycerol-phosphoric acid (p. 353), stearic acid and palmitic acid. Therefore we assume it to be an ethereal compound of choline with glycerophosphoric acid, combined as glyceride with stearic and palmitic acids:—



# INDEX

## A.

Abietic acid, 687  
 Absinth, 686  
 Aceconitic acid, 368  
 Acediamine, 250  
 Acenaphthene, 648  
 Acetal, 259  
 Acetaldehyde, 153  
 Acetamide, 210  
 Acetamidine, 250  
 Acetanilide, 442  
 Acetic acid, 175  
   anhydride, 200  
   esters, 205  
 Aceto-acetic ester, 219  
   -imido-ether, 249  
   -chlorhydrose, 385  
 Acetol, 213  
 Acetone, 162  
   bases, 165  
   chloride, 163  
   chloroform, 161  
 Acetonic acid, 286  
 Acetonitrile, 243  
 Acetonyl urea, 308  
 Acetophenone, 522  
   alcohol, 510  
   aceto-acetic ester, 548  
   carboxylic acid, 548  
 Acetoxim, 163  
 Acetoxims, 161  
 Acetoximic acids, 161, 164  
 Acetobutyric acid, 225  
   succinic acid, 222  
 Aceturic acid, 293  
 Acetyl carbinol, 213  
   carboxylic acid, 214  
   chloride, 199  
   cyanide, 200  
   sulphide, 203  
 Acetylene, 60, 61  
   dicarboxylic acid, 339  
   tetracarboxylic acid, 374  
   urea, 342  
 Aceto-acetic acid, 216, 219  
   -malonic acid, 222  
   -propionic acid, 224

Acid anhydrides, 200, 274, 316  
   chlorides, 198  
   radicals, 200  
   yellow, 467  
 Acidoxims, 249, 526  
 Aconic acid, 366  
 Aconitic acid, 367  
 Acridic acid, 674  
 Acridine, 675  
 Acrolein, 158  
 Acrylaldehyde=acrolein,  
 Acrylic acid, 190  
 Adipic acid, 331  
 Æsculetin, 558  
 Æsculin, 688  
 Alanine, 293  
 Albumen, 691  
 Albuminates, 691  
 Alcarsin, 135  
 Alcoholates, 96, 150  
 Alcohols, 87, 507  
 Aldehydes, 148, 149, 258, 511  
 Aldehyde alcohols, 252  
   ammonia, 154  
   acids, 252  
   bases, 455  
   green, 617  
 Aldehydine, 663  
 Aldol, 261  
   condensation, 155  
 Aldoxims, 152  
 Alizarin, 640  
   blue, 642  
 Alkaloids, 677  
 Alkali green, 617  
 Alkamines, 264  
 Alkaines, 264  
 Alkins, 264  
 Alkyls, 31, 45  
 Alkylens, 31, 53  
 Alkylogens, 66, 93  
 Allantoin, 341  
 Allanturic acid, 341  
 Alloxantin, 345  
 Alloxan, 344  
 Alloxanic acid, 345  
 Allophanic acid, 309  
 Allyl, 63, 71

- Allyl, alcohol, 103  
     aniline, 439  
     cyanide, 244  
     ether, 108  
     iodide, 71  
     sulphide, 111  
     acetic acid, 194  
     ethenyl carboxylic acid, 366  
     malonic acid, 338  
     succinic acid, 339  
 Allylene, 62  
 Allylin, 357  
 Aloes, 689  
 Aloetic acid, 689  
 Aloin, 689  
 Alphatoluic acid, 540  
 Aluminium-ethyl, 144  
 Amalic acid, 345  
 Amarine, 514  
 Amber, 687  
 Amic acids, 289, 317  
 Amid chlorides, 209  
 Amides, 207, 289  
 Amidines, 249, 450, 526  
 Amido-azobenzene, 467  
     -acetic acid, 291  
     -acids, 289  
     -dicyanic acid, 248  
     -glutaric acid, 364  
     -phenols, 489  
     -thiophenols, 491  
 Amidoxims, 527  
 Amines, 122, 263  
 Ammelide, 248  
 Ammeline, 248  
 Ammon-chelidonic acid, 665  
 Ammonium bases, 123, 128  
 Amygdalin, 513  
 Amygdalic acid, 514  
 Amyl alcohols, 98  
     aldehydes, 158  
 Amylenes, 58  
 Amylum, 390  
 Anethol, 520  
 Angelic acid, 193  
 Anhydrides of acids, 200, 274, 316  
     inner, 275  
 Anhydro-bases, 455, 489  
 Anilacetone, 443  
 Anilides, 437, 441  
 Anilido-glycollic acid, 442  
 Aniline, 433  
     black, 470  
     blue, 622  
     yellow, 467  
 Anilpyroracemic acid, 443  
 Aniluvitonic acid, 443  
 Anisic aldehyde, 520  
 Anisil, 632  
 Anisoil, 632  
 Anisol, 483  
 Anisic acid, 551  
 Anisyl alcohol, 511  
 Anol, 520  
 Anthracene, 637  
 Anthrachrynone, 642  
 Anthraflavic acid, 642  
 Anthramin, 637  
 Anthranil, 536  
 Anthranilic acid, 536  
 Anthranol, 638  
 Anthraquinone, 638  
 Anthraquinoline, 675  
 Anthrarufin, 642  
 Anthrapurpurin, 642  
 Anthrol, 638  
 Anthroxan aldehyde, 597  
 Anthroxanic acid, 597  
 Antimony bases, 137  
 Antipyrine, 677  
 Apophyllenic acid, 665  
 Aposorbic acid, 376  
 Arachidic acid, 188  
 Arabin, 391  
 Arabinose, 386  
 Arbutin, 688  
 Archil, 499  
 Arsines, 134  
 Arsonium compounds, 134  
 Asparagine, 363  
 Aspartic acid, 363  
 Asphaltum, 52  
 Atroglyceric acid, 561  
 Atrolactinic acid, 555  
 Atropic acid, 580  
 Atropine, 681  
 Aurantia, 440  
 Aurin, 624  
 Azalaïn, 621  
 Azelaïc acid, 333  
 Azimido-benzene, 454  
 Azo-amido compounds, 463  
 Azo-benzoic acid, 537  
 Azobenzene, 466  
 Azoconhydrine, 678  
 Azo-coloring substances, 468  
 Azo-compounds, 462  
 Azo-diphenyl blue, 470  
 Azodiphenylene, 602  
 Azophenols, 492

Azo-triple bases, 266  
 Azoxybenzene, 466  
 Azuline, 625  
 Azulmic acid, 227  
 Azylines, 467

## B.

Balsams, 687  
 Barbituric acid, 342  
 Bassorin, 391  
 Behenic acid, 172  
 Behenolic acid, 198  
 Benzal, *see* Benzylidene  
 Benzaldehyde, 513  
 Benzaldoxim, 515  
 Benzal chloride, 425  
     violet, 616  
 Benzamide, 532  
 Benzamoxalic acid, 507  
 Benzaurin, 623  
 Benzene, 414  
     sulphonic acid, 475.  
 Benzenyl amidines, 526  
     amidoxims, 527  
 Benzhydrol, 610  
 Benzhydroxamic acid, 532.  
 Benzhydroximic acid, 527  
 Benzhydryl benzoic acid, 613  
 Benzidine, 601  
 Benzil, 632  
 Benzilic acid, 632  
 Benzimido-ethers, 526  
 Benzoic acid, 531  
 Benzoaniline, 611  
 Benzoïn, 631  
 Benzonitrile, 525  
 Benzophenone, 610  
 Benz-oximido-ethers, 526  
 Benzoyl acetic acid, 547  
     aceto-acetic ester, 547  
     -aceto-carboxylic acid, 548  
     -acrylic acid, 583  
     -benzoic acid, 613  
     carbinol, 510  
     chloride, 532  
     formic acid, 546  
     glycollic acid, 533  
     propionic acid, 547  
 Benzpinacone, 633  
 Benzyl alcohol, 507  
     acetone, 524  
     amines, 508  
     -benzoic acid, 613  
     chloride, 424

Benzyl cyanide, 526  
     glycollic acid, 556  
     malonic acid, 568  
     sulphide, 508  
     toluene, 612  
 Benzylidene aceto-acetic ester, 583  
     aniline, 515  
     acetone, 575  
     malonic acid, 588  
     phenylhydrazine, 515  
 Berberine, 666  
 Berberonic acid, 666  
 Beronic acid, 665  
 Betaïne, 265  
 Beta-orcein, 499  
 Bieberich scarlets, 469  
 Biliary substances, 688  
 Bilineurine=choline, 265  
 Bilirubin, 690  
 Biliverdin, 690  
 Bismuth ethide, 147  
 Bitter almond oil, 513  
     principles, 688  
 Biuret, 309  
 Boric esters, 121  
 Boron ethyl, 138  
 Borneène, 686  
 Borneol, 686  
 Brasilin, 689  
 Brassidic acid, 196  
 Brassylic acid, 333  
 Bromal, 156  
 Bromanil, 504  
 Bromoform, 75  
 Bromopicrin, 84  
 Brucine, 681  
 Butalanine, 294  
 Butanes, 49  
 Butyl lactic acid, 287  
     chloral, 157  
 Butylenes, 58  
 Butylene glycol, 261  
 Butyraldehyde, 157  
 Butyrone, 167  
 Butyrolactone, 286  
     -carboxylic acid, 364  
 Butyronitrile, 244

## C.

Cacodylic acid, 136  
     compounds, 135  
 Caffèic acid, 586  
 Caffèine, 349



- Caffuric acid, 350  
 Camphene, 684  
 Camphor, 685  
 Camphoric acid, 686  
 Camphol=borneol, 686  
 Campholic acid, 686  
 Camphoronic acid, 687  
 Campo-bello yellow, 651  
 Caoutchouc, 687  
 Cane sugar, 387  
 Cantharidin, 689  
 Capric acid, 186  
 Capric aldehyde, 158  
 Caprone, 167  
 Caprolactone, 288  
 Caproic acid, 185  
 Caproyl alcohols, 101  
 Capryl alcohol, *see* Octyl alcohols  
 Caprylic acid, 185  
 Caprylone, 167  
 Caramel, 387  
 Carbamic acid, 300  
 Carbamides, 303, 340  
 Carbamido-phenols, 490  
 Carbanile, 444  
 Carbanilamide, 444  
 Carbanilic acid, 444  
 Carbanilide, 443  
 Carbazol, 601  
 Carbimide, 233, 301  
 Carbinol, 87  
 Carbodiimide, 247  
 Carbodiphenylimide, 450  
 Carbohydrates, 380  
 Carbon disulphide, 297  
 Carbonic acid, 276, 294  
 Carbonyl chloride, 295  
 Carbonyl urea, 309  
 Carbopyrrolic acid, 401  
 Carbopyrotartaric acid, 233  
 Carbostyryl, 671  
     carboxylic acid, 674  
 Carbostyrylic acid, 536  
 Carbothialdine, 302  
 Carboxyl, 85, 168  
 Carboxy-tartronic acid, 387  
 Carbylamines, 246  
 Carbyl sulphate, 268  
 Carminic acid, 689  
 Carmine, 349  
 Carvacrol, 495  
 Carvene, 684  
 Carvol, 686  
 Caryophyllin, 686  
 Casein, 691  
 Cassia oil, 574  
 Catechin, 560, 564  
 Catechu tannin, 564  
 Cedriret, 602  
 Cellulose, 391  
 Ceresine, 53  
 Cerotene, 60  
 Cerotin, 102  
 Cerotic acid, 188  
 Ceryl alcohol, 102  
 Cetene, 60  
 Cetyl alcohol, 102  
 Chelidonic acid, 368  
 Chloracetol, 73  
 Chloral, 158  
 Chloralides, 284  
 Chloranil, 503  
 Chloranilic acid, 504  
 Chlor-cyanogen, 230  
 Chlor-ethyl benzenes, 416  
 Chlorhydrins, 255, 354  
 Chlorformic acid, 295  
 Chlorcarbonic acid, 295  
 Chlorbenzil, 632  
 Chlormeconic acid, 338  
 Chloroform, 74  
 Chlorophyll, 690  
 Chloropicrin, 84  
 Chloroxalic ester, 319, 320  
 Chlorphenyl mustard oil, 491  
 Cholesterine, 690  
 Cholestrophane, 340  
 Cholic acid, 690  
 Choline, 265  
 Chondrin, 691  
 Chromic acid mixture, 162, 528  
 Chrysammic acid, 642  
 Chrysaniline, 676  
 Chrysanic acid, 537  
 Chrysazin, 642  
 Chrysazol, 638  
 Chrysene, 657  
 Chrysoïne, 469  
 Chrysoidines, 464, 467  
 Chrysolin, 629  
 Chrysophanic acid, 643  
 Chrysophenol, 676  
 Chrysoquinone, 658  
 Cinchomeric acid, 665  
 Cinchonidine, 680  
 Cinchonine, 680  
 Cinchoninic acid, 673  
 Cinnamon, 577

Cinnamene, 572  
 Cinnamic acid, 576  
     aldehyde, 574  
 Cinnamone, 575  
 Cinnamyl alcohol, 574  
     formic acid, 582  
 Cinnoline, 675  
 Citraconic acid, 337  
 Citramide, 374  
 Citramalic acid, 364  
 Citrene, 684  
 Citric acid, 373  
 Cochineal, 689  
 Codeine, 679  
 Coeroulignone, 602  
 Coeroulin, 629  
 Collidine, 663  
     dicarboxylic acid, 666  
 Collodion, 392  
 Colophony, 687  
 Comenic acid, 368  
 Comenamic acid, 664  
 Condensation, 56, 154  
 Conhydrine, 679  
 Coniferine, 521  
 Coniferyl alcohol, 521  
 Conine, 678  
 Convolvulin, 688  
 Conylene, 678  
 Conyryne, 663  
 Copaiva oil, 685  
 Corindine, 660  
 Cotarnine, 680  
 Coumarilic acid, 586  
 Coumarin, 583, 585  
 Coumarinic acid, 586  
 Coumaron, 586  
 Coumaric acid, 584  
 Coumazon compos, 551  
 Creasote, 481, 500  
 Creatine, 313  
 Creatinine, 314  
 Creosol, 500  
 Cresols, 493  
 Cresorcin, 499  
 Cresotinic acids, 552  
 Crocein, 652  
 Crotaconic acid, 338  
 Croton aldehyde, 159  
 Croton-chloral, 157  
 Croton oil, 194  
 Crotonic acids, 192  
 Crotonylene, 60  
 Crotyl alcohol, 104  
 Cryptidine, 667

Cubebs, oil of, 685  
 Cumene, 418  
 Cumenol, 494  
 Cumic acids, 545  
     aldehyde, 518  
 Cumidines, 453  
 Cuminalcohol, 509  
     oil, 495  
 Cuminil, 632  
 Cuminoïn, 632  
 Cuminol=cumic aldehyde, 518  
 Cumylic acid=durylic acid, 545  
 Curcumin, 689  
 Cyammelide, 233  
 Cyanogen, 227  
     carbonic acid, 295  
     chloride, 239  
     iodide, 230  
     sulphide, 239  
 Cyan-acetic acid, 212  
     -amide, 233  
     -anilide, 450  
     -conine, 244  
     -ethine, 243  
     -etholins, 233  
     -guanidine, 248  
     -methine, 243  
 Cyanic acid, 233  
     esters, 235  
 Cyanides, metallic, 230  
 Cyanuric acid, 234  
     esters, 237  
 Cymenes, 419

## D.

Dambose, 387  
 Daphnetin, 588  
 Daphnin, 588  
 Daturin=atropin, 681  
 Decyl alcohol, 102  
 Dehydracetic acid, 220  
 Dehydromucic acid, 398  
 Desoxalic acid, 376  
 Desoxybenzoïn, 632  
 Dextrine, 391  
 Dextrose, 384  
 Diacetamide, 211  
 Diacetic acid. See Aceto-acetic acid.  
 Diacetone alcohol, 166, 213  
 Diacetoneamine, 165  
 Diaceto-acetic ester, 221  
     -succinic acid, 223  
 Diethyl, 49  
     -fumaric acid, 338

- Daldan, 261  
 Diallyl, 63  
   -acetic acid, 198  
   malonic acid, 338  
 Dialuramide, 343  
 Dialuric acid, 343  
 Diamido-benzenes, 453  
 Diamines, 263  
 Diamylene, 59  
 Diastase, 382  
 Diaterebic acid, 365  
 Diaterpenylic acid, 365  
 Diazoamidobenzene, 460  
 Diazobenzoic acids, 538  
 Diazo-compounds, 459  
 Dibenzoyl, 632  
   acetic acid, 549  
   methane, 549  
   succinic acid,  
 Dibenzyl, 630  
   carboxylic acids, 634  
   glycollic acid, 634  
 Dicarboxylic tetracarboxylic acid, 374  
 Dichlorhydrins, 354  
 Dicyanogen, 227  
 Dicyanamide, 248  
 Dicyandiamide, 248  
 Dicyandiamidine, 248  
 Digallic acid, 563  
 Diglycollic acid, 278  
 Diglycolamidic acid, 293  
 Diisatogen, 593  
 Diketones, 260, 252, 503, 524  
 Dilituric acid, 342  
 Dimethyl, 49  
   aniline, 438  
   fumaric acid, 338  
   glyoxim, 166  
   -phenylene green, 470  
 Dinitro-aceto-nitrile, 245  
 Dinitroparaffins, 82  
 Dioxindol, 594  
 Dioxybenzophenone, 611  
 Dioxybutyric acid, 360  
 Dioxymalonic acid, 369  
 Dioxysuccinic acid, 369  
 Dioxytartaric acid, 378  
 Diphenine, 468  
 Diphenic acid, 604  
 Diphenols, 602  
 Diphenyl, 600  
   acetic acid, 611  
   glycollic acid, 612  
 Diphenylamine, 439  
   blue, 623  
 Diphenyl-benzene, 606  
   -carbinol, 610  
   carboxylic acids, 603  
   -diacetylene, 574  
   -ethane, 611  
   -ethylene, 611  
   -glyoxims, 632  
 Diphenylimide, 601  
 Diphenyl-succinic acid, 633  
   ketone, 610  
   methane, 609  
 Diphenylene acetic acid, 605  
   derivatives, 604  
   glycollic acid, 605  
   ketone, 604  
     oxide, 611  
   methane, 605  
 Diphenylin, 601  
 Diphenylol, 602  
 Dipropargyl, 63  
 Dipyridine, 662  
 Dipyridyl, 662  
   carboxylic acid, 667  
 Disacryl, 159  
 Disazo-compounds, 465  
 Disulphoxides, 474  
 Ditolyl, 606  
 Ditolylamine, 453  
 Ditolyl methane, 613  
 Diureides, 345  
 Dulcitol, 377  
 Durene, 418  
 Durylic acid, 545  
 Dynamite, 353  
  
 E.  
 Elaidic acid, 196  
 Ellagic acid, 562  
 Emerald green, 493  
 Emodin, 643  
 Emulsin, 514  
 Eosin, 629  
 Epichlorhydrin, 355  
 Epiphydrin-carboxylic acid, 353  
 Erucic acid, 196  
 Erythrin, 560  
 Erythrite, 369  
 Erythritic acid, 369  
 Erythro-oxy-anthraquinone, 640  
 Esters, 105, 114, 203  
 Ethal, 102  
 Ethane, 49  
 Ethenyl amidine, 250  
   -amido-thiophenols, 491

Ethenyl tricarboxylic acid, 366  
 Ether anæstheticus, 667  
 Ethers, compound, 105, 203  
     mixed, 105  
     simple, 105  
 Ether-acids, 114  
 Ethereal oil, 684  
 Ethidene compounds, 259  
     chloride, 69  
     malonic acid, 337  
     sulphonic acids, 268  
 Ethyl. See Dimethyl.  
     alcohol, 94  
     aldoxim, 154  
     amine, 127  
     benzoic acids, 543  
     carbonic acid, 295  
     chloride, 66  
     ether, 107  
     hydride. See Ethane.  
     iodide, 68  
     nitrite, 116  
     sulphide, 110  
     sulphanilic acid, 120  
     tartaric acid, 364  
 Ethylene, 57  
     chloride, 69  
     cyanide, 257  
     diamine, 263  
     glycol, 256  
     oxide, 257  
     lactic acid, 281  
     sulphonic acids, 266  
 Eucalyn, 387  
 Euchrone, 571  
 Eugenol, 587  
 Eupittonic acid, 625  
 Euthiochronic acid, 498  
 Euxanthonic acid, 689  
 Euxanthin, 689  
 Everninic acid, 561

## F.

Fats, 195, 358  
 Fatty acids, 168, 171  
 Fermentation, 382  
 Ferulic acid, 586  
 Fibrin, 691  
 Fichtelite, 658  
 Flavaniline, 673  
 Flavenol, 673  
 Flavol, 638  
 Flavoline, 673  
 Flavopurpurin, 642

Fluoranthene, 657  
 Fluorbenzene, 424  
 Fluorbenzoic acid, 535  
 Fluorene, 605  
     alcohol, 605  
 Fluoresceïn, 628  
 Fluorescin, 629  
 Formal, 256  
 Formamide, 210  
 Formamidine, 250  
 Formanilide, 441  
 Formic acid, 173  
     aldehyde, 152  
 Form-imido-ethers, 249  
 Formonitrile, 243  
 Formyl tricarboxylic acid, 366  
 Frangulinic acid, 642  
 Fruit essences, 205  
     sugar, 385  
 Fuchsine, 620  
 Fulminuric acid, 245  
 Fumaric acid, 335  
 Furfuran, 395  
 Furfuryl group, 395  
 Furfurol, 395  
 Furoïn, 397  
 Furonic acid, 396  
 Fusel oil, 95, 99

## G.

Gaidinic acid, 195  
 Galactose, 386  
 Galleïn, 629  
 Gallesine, 384  
 Gallic acid, 362  
 Garancin, 641  
 Gaultheria procumbens, 549  
 Gelatines, 690  
 Gentisin, 689  
 Gentisinic acid, 558  
     aldehyde, 520  
 Gluconic acid, 378  
 Glutaconic acid, 337  
 Glutaminic acid, 364  
 Glutaric acid, 330  
 Gluten, 693  
 Glutin, 691  
 Glycerol, 352  
     ethers, 357  
 Glyceryl chloride, 76  
 Glycerides, 357  
 Glyceric acid, 359  
 Glycidic acid, 356  
 Glycide compounds, 355



Glycine or Glycocoll, 291  
 Glycocholic acid, 690  
 Glycocoll, 291  
 Glycocyamine, 312  
 Glycogen, 390  
 Glycolide, 278  
 Glycollic acid, 276  
 Glycols, 254, 260  
 Glycoluric acid, 308  
 Glycolyl, 276  
 Glycolyl urea, 307  
 Glycolyl aldehyde, 258  
 Glucoses, 384  
 Glucosides, 383  
 Glucosin, 279  
 Glycouril, 342  
 Glycuronic acid, 378  
 Glyoxal, 258, 279  
 Glyoxal ethylin, 280  
 Glyoxalin, 279  
 Glyoxalic acid=Glyoxylic acid, 280  
 Glyoxims, 161, 164, 279  
 Glyoxyl urea, 341  
 Glyoxylic acid, 280  
 Granulose, 390  
 Guaiacol, 496  
 Guanidines, 280, 312, 449  
 Guanine, 348  
 Guanamines, 252  
 Guanyl urea, 248  
 Gum resins, 687  
 Gutta percha, 687  
 Gun cotton, 392

## H.

Hæmatein, 689  
 Hæmatin, 694  
 Hæmatoxylin, 689  
 Hæmin, 694  
 Hæmoglobin, 693  
 Haloid anhydrides, 170, 198  
 Halogen esters, 114, 254  
 Helianthine, 469  
 Helicin, 510  
 Hemimellitic acid, 570  
 Hemipinic acid, 569  
 Heptanes, 50  
 Heptoic acids, 185  
 Heracleum oil, 181, 206  
 Herapathite, 680  
 Hesperidin, 688  
 Hesperitic acid, 586  
 Hexanes, 50

Hexoic acids, 185  
 Hexoylene, 63  
 Hexyl alcohols, 101  
 Hipparaffin, 533  
 Hippuric acid, 533  
 Homoprotocatechuic acid, 560  
 Homo-pyrocatechuic acid, 499  
 Hyænic acid, 172  
 Hydantoic acid, 308  
 Hydantoin, 308  
 Hydracrylic acid, 285  
 Hydramines, 264  
 Hydranthranol, 638  
 Hydrazines, 129, 471  
 Hydrazo-benzene, 468  
     benzoic acid, 538  
 Hydrindic acid, 553  
 Hydrindo-naphthene, 644  
 Hydroatropic acid, 545  
 Hydrobenzamide, 514  
 Hydrobenzoin, 631  
 Hydrocarbostyrl, 544  
 Hydrocinnamide, 574  
 Hydrocinnamic acid, 543  
 Hydrocoumarin, 554  
 Hydrocoumaric acid, 554  
 Hydroferulic acid, 561  
     fluoric " 228  
     cyanic " 228  
     caffeic " 561  
     meconic " 338  
     phlorol, 500  
     sorbic acid, 198  
     umbellic " 561  
     rubianic " 228

Hydroxamic esters, 527  
 Hydroxy acids=Oxy acids  
 Hyoscine, 682  
 Hyoscyamine, 682  
 Hypogæic acid, 195  
 Hypoxanthine=sarcine, 349

## I.

Idrialin, 658  
 Idryl, 657  
 Imesatin, 595  
 Imide chlorides, 209  
 Imides, 308  
 Imido-ethers, 248, 526  
     -thio-carbonic acids, 309  
     -thio-ethers, 249  
 Indazol, 580  
 Indican, 592, 598  
 Indigo, 597

Indigo, carmine, 600  
     purpurine, 599  
 Indigotin, 597  
     white, 599  
 Indin, 599  
 Indirubin, 593  
 Indoanilines, 506  
 Indogenides, 593  
 Indoin, 599  
 Indol, 589  
 Indolin, 590  
 Indophenin, 595  
 Indophenols, 505  
 Indoxanthic acids, 593  
 Indoxyl, 592  
 Indoxylic acid, 592  
 Indulines, 469  
 Inosite, 386  
 Inuline, 390  
 Invert sugar, 385  
 Iodine, green, 621  
 Iodoform, 75  
 Ipomic acid, 688  
 Iridolin, 672  
 Isatin, 594  
 Isatinic acid, 546  
 Isatogenic acid, 593  
 Isatoxim, 596  
 Isatropic acid, 581  
 Isatid, 595  
 Isethionic acid, 267  
 Isobenzil, 632  
 Isobutyric acid, 182  
 Isocapro lactone, 288  
 Isocyanides, 246  
 Isocyanic acid, 233  
 Isocyanuric acid, 234  
 Isodiphenic acid, 604  
 Isodulcitol, 378  
 Isoferulic acid, 586  
 Isoindol, 523  
 Isonicotine, 662  
 Isonicotinic acid, 664  
 Isonitriles, 246  
 Isonitroso compounds, 152, 485  
 Isonitroso-acetone, 162  
     acids, 171  
     acetic acids, 178  
 Isophthalic acid, 566  
 Isopropyl alcohol, 97  
     iodide, 68  
 Isopurpuric acid, 489  
 Iso-orcin, 499  
 Isosuccinic acid, 329  
 Isothio-acetamide, 209, 442

Isothio-cyanic acid, 237, 238  
 Isothio-ureas, 448  
 Isovanillin, 521  
 Isuret, 250, 305  
 Itaconic acid, 338  
 Itamalic acid, 364

## J.

Jalapin, 688

## K

Kairine, 671  
 Kairolin, 670  
 Ketines, 164  
 Ketol, 591  
 Ketones, 148, 160, 521  
 Ketonic acids, 214, 334, 546, 582  
 Kino-tannin, 564  
 Kynurenic acid, 674  
 Kynuric acid, 536  
 Kynurine, 671

## L.

Lactams, 541  
 Lactamides, 289  
 Lactic acids,  
 Lactides, 275, 282  
 Lactimides, 289  
 Lactims, 541  
 Lactonic acid, 378  
 Lactones, 275, 276  
 Lactonic acids, 365  
 Lactose, 388  
 Lacturic acid, 308  
 Lactyl chloride, 283  
 Lactyl urea, 308  
 Laevulinic acid, 224  
 Laevulose, 385  
 Lauric aldehyde, 158  
     acid, 187  
 Laurene, 167  
 Lead tri-ethyl, 147  
 Lecanoric acid, 560  
 Lecithin, 265  
 Legumin,  
 Lepargylic acid, 333  
 Lepidine,  
 Leucaniline, 623  
 Leucaurollic acids, 619  
 Leucic acid, 288  
 Leucine, 294  
 Leucomalachite green, 616  
 Leuco-rosolic acid, 625  
 Lichinine, 390

Lignoceric acid, 172  
 Ligroine, 52  
 Linoleic acid, 196  
 Litmus, 499  
 Lophine, 514  
 Luteoline, 560  
 Lutidine, 663  
 Lutidinic acid, 665

## M.

Maclurin, 560, 564  
 Magdala red, 650  
 Malachite green, 617  
 Malamide, 362  
 Maleic acid, 334, 335  
 Malic acid, 361  
 Malonyl urea, 342  
 Maltose, 389  
 Mandarin yellow, 676  
 Mandelic acid, 552  
 Mannide, 377  
 Mannitan, 377  
 Mannitic acid, 378  
 Mannitol, 376  
 Margaric acid, 187  
 Marsh gas, 48  
 Mauvaniline, 470  
 Mauvéine, 470  
 Meconine, 569  
 Meconic acid, 368  
 Meconinic acid, 568  
 Melamine, 248  
 Melampyrine=Dulcitol, 377  
 Melene, 60  
 Melilotic acid, 554  
 Melissic acid, 188  
 Melissyl alcohol, 103  
 Melitose, 388  
 Melezitose, 389  
 Mellimide, 571  
 Mellitic acid, 570  
 Mellophanic acid, 570  
 Menthene, 683  
 Menthol, 686  
 Mercaptans, 108  
 Mercaptides, 109  
 Mercury-ethide, 144  
 Mesaconic acid, 338  
 Mesidic acid, 567  
 Mesidine, 453  
 Mesitylene, 415  
 Mesitylenic acid, 542  
 Mesityl oxide, 165  
 Mesitylol, 494  
 Mesole, 77

Mesorcin, 500  
 Mesoxalic acid, 323  
 Mesoxalyl urea, 344  
 Mesotartaric acid, 372  
 Mataldehyde, 154  
 Metallo-organic compounds, 139  
 Methacrylic acid, 193  
 Methane, 48  
 Methionic acid, 266  
 Methenyl amidine, 250  
     tricarboxylic acid, 366  
 Methyl aldehyde, 152  
     alcohol, 94  
 Methylamine, 126  
 Methyl-anthracene, 643  
     chloride, 66  
     cyanide, 246  
     ether, 107  
     glyoxim, 164  
     iodide, 68  
     green, 622  
     indol, 590  
     ketol, 590  
     orange, 440  
     umbelliferon, 587  
     violet, 622  
     quinolic acid, 666  
 Methylene, 56  
     blue, 444  
     chloride, 72  
     derivatives, 256  
 Milk sugar, 388  
 Mirbane oil, 426  
 Morin, 564  
 Moringa-tannin, 564  
 Morphine, 679  
 Mucobromic acid, 336  
 Mucochloric acid, 337  
 Muconic acid, 366  
 Murexan, 343  
 Murexide, 346  
 Muscarine, 265  
 Mycose, 389  
 Myosin, 693  
 Myricyl alcohol, 103  
 Myristic aldehyde, 158  
 Myrisitic acid, 187  
 Myristone, 167  
 Myronic acid, 241  
 Myrosine, 241  
 Mucic acid, 379  
 Mustard oil, 238

## N.

Naphtha, 51  
 Naphthalene, 645

Naphthalene, yellow, 551  
     red, 650  
 Naphthalidine = naphthylamine.  
 Naphthalic acid, 654  
 Naphthalizarine, 653  
 Naphthene, 52  
 Naphthoic acid, 654  
 Naphthols, 651  
 Naphthol blue, 653  
 Naphthoquinone, 653  
 Naphthylamine, 650  
 Narceine, 679  
 Narcotine, 679  
 Neurine, 265  
 Nicotidene, 662  
 Nicotine, 679  
 Nicotinic acid, 664  
 Nigrosine = azodiphenyl blue.  
 Nitranilic acid, 504.  
 Nitriles, 241, 524  
 Nitroparaffins, 79  
 Nitro-acetonitrile, 244  
 Nitrobenzene, 436  
 Nitrococcic acid, 690  
 Nitroform, 83  
 Nitromethane, 79  
 Nitroglycerol, 353  
 Nitrolic acids, 80, 81  
 Nitrophenols, 487  
 Nitropropionic acid, 180  
 Nitroprussides, 232  
 Nitroso-amines, 128  
     naphthols, 437 653  
     phenol, 486  
     derivatives, 78, 426  
 Nitro-compounds, 79, 426  
 Nonoic acid, 185  
 Noropianic acid, 569

## O.

Octane, 50  
 Octyl alcohol, 102  
 Oenanthal, 158  
 Oenanthane, 167  
 Oenanthylic alcohol, 102  
     acid, 185  
 Oils, drying, 196, 358  
     fatty, 186, 358  
 Olibene, 684  
 Oledines, 53  
 Olfiant gas, 57  
 Oleic acids, 187, 195  
 Opianic acid, 569  
 Opium, 679  
 Orcein, 499

Orcin, 498  
 Orsellinic acid, 560  
 Orthoformic ester, 352, 483  
 Ortho-carbonic ester, 368  
 Oxalan, 341  
 Oxalmethylin, 280, 321  
 Oxalic acid, 318  
 Oxaluric acid, 341  
 Oxalyl urea, 340  
 Oxamethane, 321  
 Oxamide, 320  
 Oxamic acid, 321  
 Oxamidine, 321  
 Oxamidines, 250, 527  
 Oxanilide, 443  
 Oxanilic acid, 443  
 Oxanthranol, 638  
 Oxatolyl acid, 634  
 Oxims = aldoxims.  
 Oximido-compounds, 78, 152  
     esters, 321, 527  
 Oxindol, 591  
 Oxy-ethylene bases, 264  
     benzoic acid, 549  
     coumarin, 587  
     quinolines, 670  
     quinolic acid, 665  
     cinchoninic acid, 674  
     citric acid, 376  
     chrysazin, 642  
     cyanides, 151, 161, 271  
     glutaric acid, 366  
     malonic acid, 360  
     methyl-benzoic acids, 552  
     methylene, 152  
     neurine = betaine  
     phenic acid, 495  
     phenyl-acetic acid, 552  
     propyl benzoic acid, 557  
     phthalophenone, 627  
     phthalic acids, 568  
     acids, 269, 548  
     tetraldine, 159  
     uvitic acid, 568  
     cinnamic acids, 557  
 Ozokerite, 53

## P.

Palmitin, 558  
 Palmitic aldehyde, 158  
     acids, 187  
 Palmitolic acid, 198  
 Palmitone, 167  
 Palmitoxylic acid, 198  
 Papaverine, 679



- Parabanic acid, 340  
 Paraconine, 157  
 Paraconic acid, 364  
 Paracyanogen, 228  
 Paraffin, 48, 52  
 Paraldehyde, 154  
 Paraldol, 261  
 Param, 248  
 Paramide, 571  
 Parietic acid, 643  
 Parvoline, 660  
 Pelargonic acid, 185  
 Pentane, 49  
 Pentinic acid, 225  
 Peonine, 625  
 Pepsine, 692  
 Peptones, 692  
 Peru balsam, 532  
 Petroleum, 51  
 Peppermint oil, 686  
 Phaseomannite = inosite  
 Phenacetolin, 482  
 Phenanthrene, 655  
 Phenanthraquinone, 656  
 Phenanthridine, 675  
 Phenanthroline, 675  
 Phenetol, 483  
 Phenol-ethers, 483  
 Phenoquinone, 504  
 Phenols, 478, 481  
 Phenolphthalein, 628  
 Phenol-sulphonic acids, 492  
 Phenose, 502  
 Phenyl acetic acid, 540  
     acetone, 524  
     acetylene, 573  
     alanine, 543  
     amidines, 450  
     benzoic acid, 603  
     butyro-lactone, 557  
     carbonate, 452  
     carbylamine, 445  
     cinnamic acid, 634  
     crotonic acid, 581  
     ethers, 624  
     ethylene, 572  
     glycerol, 511  
     glyceric acid, 561  
     glycidic acid, 557  
     glycollic acid, 483, 552  
     glycocoll, 442  
     glyoxim, 523  
     glyoxalic acid, 546  
     guanidine, 449  
     hydantoin, 444  
 Phenyl hydracrylic acid, 556  
     hydrazine, 473  
     imido butyric acid, 443  
     itamalic acid, 568  
     isocyanide, 445  
     isocyanide, 445  
     oxyacrylic acids, 557  
     lactic acid, 556  
     phosphine, 451  
     mustard oil, 445  
         glycollide, 447  
     propionic acid, 581  
     paraconic acid, 568  
     pyridine, 663  
     propionic acid, 543  
     quinoline, 673  
     styceric acid, 561  
     sulphide, 484  
     sulphone, 476  
     sulph-hydantoin, 449  
     thio-hydantoin, 449  
         urea, 447  
     thiurethanes, 446  
     tolyl, 606  
     urea, 444  
     urethanes, 444  
 Phloramine, 501  
 Phloretin, 688  
 Phloretic acid, 555  
 Phlorizidin, 688  
 Phenyl-hypo-phosphorous acid, 451  
 Phloroglucin, 501  
 Phlorol, 491  
 Phloron, 505  
 Phœnicin-sulphuric acid, 599  
 Phorone, 165  
 Phosgene, 295  
 Phosphenyl chloride, 451  
 Phosphin, 676  
 Phosphines, 131, 451  
 Phosphinic acids, 122  
 Phosphoric esters, 121, 482  
 Phospho-benzene, 451  
 Phosphoric acids, 121  
 Photogene, 52  
 Phrenitic acid, 570  
 Phthalanile, 443  
 Phthaleins, 627  
 Phthal-green, 629  
 Phthalic acid, 565  
 Phthalic aldehyde, 518  
 Phthalid, 552  
 Phthalideins, 628  
 Phthalidins, 628, 638  
 Phthalids, 625

Phthalins, 628, 638  
 Phthalophenone, 626  
 Phthalyl acetic acid, 548  
 Phthalyl alcohol, 509  
 Phthalyl hydroxamic acid, 566  
 Phycite, 319  
 Picamar, 501  
 Picene, 658  
 Picolinic acid, 664  
 Picoline, 663  
 Picoline carboxylic acids,  
 Picramide, 436  
 Picramic acid, 481  
 Picric acid, 488  
 Picro-cyaminic acid, 489  
 Picroerythrin, 560  
 Picrotoxin, 689  
 Pimaric acid, 687  
 Pimelic acid, 332  
 Pinacones, 161, 262, 633  
 Pinacoline, 161, 167, 633  
 Pinacolyl alcohol, 101  
 Pinite, 375  
 Piperhydronic acid, 588  
 Piperidine, 677  
 Piperic acid, 588  
 Piperine, 678  
 Piperonal, 521  
 Piperonyl alcohol, 511  
 Piperylene, 678  
 Piperonylic acid, 559  
 Pittical, 625  
 Pivalic acid = Trimethyl acetic acid.  
 Polyglycerols, 359  
 Polyglycols, 258  
 Polymerization, 56, 151  
 Populin, 510  
 Porissic acid = Euxanthic acid.  
 Propane, 49  
 Propargyl alcohol, 104  
 Propenyl-benzoic acid, 557  
 Propenyl-tricarboxylic acid, 366  
 Propidene acetic acid, 194  
 Propidene chloride, 73  
 Propiolic acid, 197  
 Propionamide, 211  
 Propione, 167  
 Propionic acid, 178  
 Propionitrile, 243  
 Propionyl chloride, 200  
 Propiophenone, 523  
 Propio-propionic acid, 225  
 Propyl alcohols, 96  
 Propyl chlorides, 66  
 Propylene, 53, 57

Propylene-oxy-carboxylic acid, 356  
 Protagon = Lecithin.  
 Protein substances, 691  
 Protocatechuic acid, 558  
 Protocatechuic aldehyde, 520  
 Pseudo-cumene, 417  
   -indoxyl, 593  
   -isatin, 594  
   -isatoxim, 596  
   -nitrols, 82  
   -purpurin, 644  
 Ptomaines, 265  
 Pulvic acid, 635  
 Purpuric acid, 346  
 Purpurin, 642  
 Purpur-oxanthin, 642  
 Purrée, 689  
 Pyrene, 657  
 Pyridine, 662  
 Pyridine-carboxylic acids, 664  
 Pyridine-dicarboxylic acids, 665  
 Pyrocatechin, 495  
 Pyrocinchonic acid, 338  
 Pyrocomenic acid, 368  
 Pyrogallol, 500  
 Pyrogallol-carbonic acid, 562  
 Pyrogallic acid, 500  
 Pyroglutaminic acid, 364  
 Pyromellitic acid, 570  
 Pyromucic acid, 223  
 Pyroxylin, 392  
 Pyrrocol, 402  
 Pyrrol, 399  
 Pyrrol-carboxylic acid, 401  
 Pyrrolin, 402  
 Pyruvil, 341

## Q.

Quercite, 374  
 Quercitin, 688  
 Quercitrin, 688  
 Quinaldic acid,, 673  
 Quinaldine, 671  
 Quinic acid, 564  
 Quinazol, 676  
 Quinhydrone, 504  
 Quinine, 680  
 Quinisatin, 548  
 Quinisatinic acid, 548  
 Quinizarin, 642  
 Quinazine compounds, 676  
 Quinolic acid, 665  
 Quinoline, 669  
 Quinone-carboxylic acid, 558  
 Quinone chlorimides, 505

Quinones, 502, 503  
Quinoxalins, 676

## R.

Radicals, 9, 30, 46, 200  
Rape-seed oil, 196  
Resacetophenone, 523  
Resocytamin = Methyl-umbelliferon, 587  
Resorcin, 496  
Resorcinol-phthalein, 628  
Resorcyl aldehyde, 520  
Resorcylic acid, 558  
Retene, 658  
Retisten, 658  
Rheic acid = chrysophanic acid.  
Ricinoleic acid, 196  
Roccellic acid, 333  
Rocellin, 652  
Roman oil of cumin, 194  
Rosaniline blue, 622  
Rosanilines, 618, 619  
Rosolic acid, 625  
Ruberythric acid, 640  
Rubidine, 660  
Rubin, 621  
Rue, oil of, 167  
Rufigallic acid, 562, 643  
Rufopin, 642  
Rufol, 638

## S.

Saccharic acid, 375  
Saccharates, 381  
Saccharin, 375  
Saccharon, 375  
Saccharose, 387  
Safflower, 689  
Saffranine, 469  
-surrogate, 493  
Salicin, 510  
Salicylic acid, 549  
aldehyde, 519  
Saligenin, 510  
Santoic acid, 689  
Santonin, 689  
Saponin, 688  
Saponification, 114  
Sarcine, 349  
Sarcosine, 293  
Scarlet, 469  
Schererite, 658  
Schweinfurt's green, 177  
Sebacic acid, 333  
Seignette salt, 371

Serin, 360  
Shellac, 687  
Skatole, 591  
Silico-benzoic acid, 451  
Silicon-ethide, 138  
Silicononyl alcohol, 139  
Silico-propionic acid, 139  
Sinamine = allycyanide,  
Sinapic acid, 682  
Sinapine, 682  
Sinapoline, 306  
Sincaline = choline,  
Soaps, 186  
Solar oil, 52  
Sorbic acid, 198  
Sorbine, 386  
Sorbite, 377  
Sparteine, 679  
Spermaceti, 206  
Starch, 380  
Stearic acid, 187  
aldehyde, 158  
Stearin, 187  
Stearoleic acid, 198  
Stearone, 167  
Stearoxylic acid, 198  
Stib-ethyl, 137  
Stibines, 137  
Stilbene, 630  
carboxylic acid, 634  
Storax, 576  
Strychnine, 681  
Styicerine, 511  
Styphnic acid, 497  
Styracine, 577  
Styrene, 574  
Styrolene, 572  
alcohol, 509  
Styryl alcohol, 574  
Suberic acid, 333  
Suberone, 333  
Succinamic acid, 327  
Succinic acid, 324  
Succinimide, 326  
Succino-succinic ether, 223  
Sugar, 384  
Sulph. See also Thio  
Sulphamides, 128, 473  
Sulphanilic acid, 477  
Sulphines, 112  
Sulphinic acids, 112, 474  
Sulphourethanes, 302, 446  
Sulpho-acetic acid, 212  
-acids, 119, 211, 473  
-benzide, 474

Sulpho-carbamic acid, 301, 446

- carbamide, 308
- carbanile, 445
- carbanilide, 447
- carbonic acid, 299
- hydantoins, 312

Sulphones, 110

Sulphoxides, 110

Sulph-urea, 309

Sycoceryl alcohol, 509

Sylvic acid, 687

## T.

Tannin, 563

Tartaric acid, 369

Tartramide, 371

Tartrellic acid, 370

Tartronic acid, 360

Tartronyl urea, 343

Taurine, 267

Tauro-betaïne, 268

- cholic acid, 690

Teraconic acid, 339

Teracrylic acid, 195

Terebene, 683

Terebilenic acid, 365

Terephthalic acid, 566

Terpenes, 682

Terpenylic acid, 365

Terpine, 684

Terpilene, 684

Tetramethylene derivatives, 394

Tetraphenyl ethers, 634

Tetrazo-compounds, 465

Tetrazones, 130, 472

Tetrinic acid, 225

Tetrol, 393

Tetrolic acid, 197

Thebaïne, 679

Theïne, 349

Theobromic acid, 188

Theobromine, 349

Thiacetic acid, 203

Thialdine, 157

Thienyl. See Thiophene

Thio-acetanilide, 442

- acetic acid, 203
- acids, 202
- alcohols, 108
- aldehydes, 157
- amides, 210
- carbamic acids, 301, 302, 445
- carbonic acids, 299, 300
- cyanic acids, 237
- cymene, 495

Thio-diphenylamine, 440

- ethers, 108

-hydantoins, 312, 449

- methanes, 302, 446

Thionuric acid, 343

Thiophene, 398

Thiophenol, 483

Thio-sinamine, 311

- tolene, 399

Thymene, 684

Thymo-hydroquinone, 500

Thymoïl, 505

Thymol, 494

Thymo-quinone, 505

Tiglic acid, 194

Tin ethide, 145

Tolane, 630

Tolylene alcohol, 509

Tolu balsam, 532

Toluene, 414

Tolu-hydroquinone, 500

Toluic acids, 538

- aldehyde, 517

Toluidine, 452

Tolunitrile, 526

Toluquinolines, 671

Toluquinone, 504

Toluylene, 630

- blue, 470

diamine, 454

glycols, 631

hydrate, 632

- red, 470

Tolyl alcohols, 508

Trehalose = mycose.

Triacetamide, 211

Triacetonamine 166

Triacetonine, 166

Tribenzoyl methane, 548

Tricarballic acid, 367

Trichlorhydrin, 355

Trichloracetic acid, 284

Tridecylic acid, 187

Trimellitic acid, 569

Trimesic acid, 569

Trimethyl acetic acid, 184

- amine, 128

carbinol, 98

Trimethylene bromide, 74

Trimethylene derivatives, 393

Trinitroacetonitrile, 245

Trioxymethylene, 153

Triphenyl acetic acid, 615

Triphenylamine, 441

Triphenyl benzene, 606



Triphenyl-carbinol, 615  
     methane, 614  
     methane carboxylic acid, 626  
 Tropæolines, 465, 469  
 Tropeines, 682  
 Tropic acid, 555  
 Tropidene, 679  
 Tropine, 682  
 Turpentine oil, 683  
 Tyrosine, 554

## U.

Umbellic acid, 587  
 Umbelliferon, 587  
 Undecylenic acid, 195  
 Undecylic acid, 186  
 Undecolic acid, 198  
 Uramido-benzoic acid, 537  
 Uramil, 343  
 Ureïdes, 307, 340, 345  
 Urethanes, 300  
 Uvitonic acid, 666  
 Uvinic acid, 223  
 Uvitic acid, 567

## V.

Valeraldehydes, 158  
 Valeric acids, 183  
 Valeridine, 158  
 Valeritrine, 158  
 Valerolactone, 287  
 Valerylene, 63  
 Vallylene, 63  
 Vanillin, 521  
     alcohol, 511

Vanillic acid, 559  
 Vaseline, 53  
 Veratric acid, 599  
 Veratrine, 682  
 Veratrol, 496  
 Victoria green, 617  
     orange, 493  
 Vinyl 69  
     alcohol, 103  
     -ethyl ether, 108  
 Violet-aniline, 470  
 Violuric acid, 343  
 Viridin, 617  
 Vulpic acid, 635

## W.

Wax, 207  
 Winter-green oil, 549

## X.

Xanthic acids, 298  
 Xanthine, 349  
 Xanthoquinic acid, 674  
 Xenylamine, 601  
 Xeronic acid, 339  
 Xylenols, 494  
 Xylenes, 415  
 Xylic acids, 542  
 Xylidic acid, 567  
 Xylidines, 453  
 Xyloquinone, 504

## Z.

Zinc ethide, 142  
     methide, 142



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